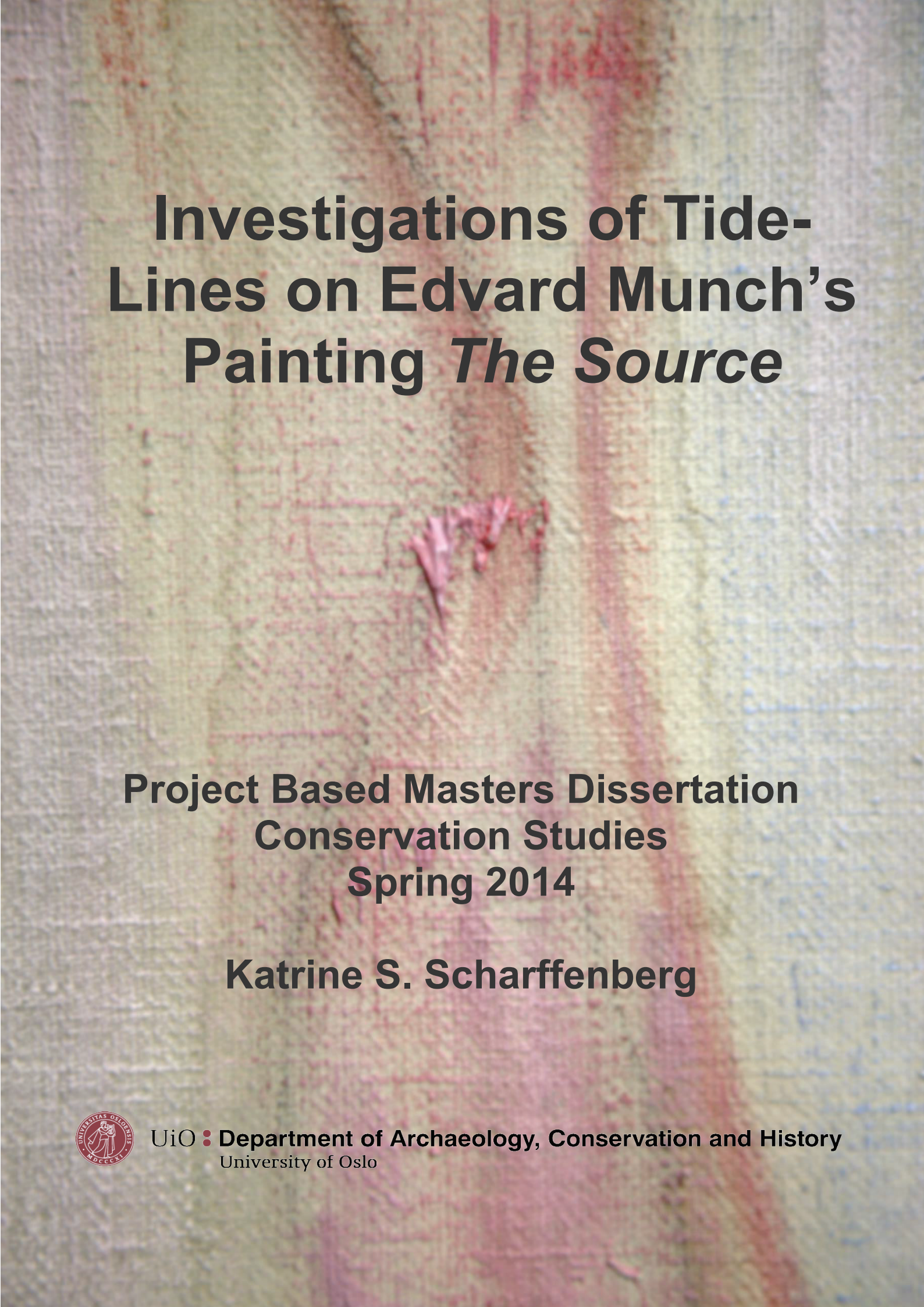

# Investigations of Tide-Lines on Edvard Munch's Painting *The Source*

**Project Based Masters Dissertation**
**Conservation Studies**
**Spring 2014**

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2014

Tide-Lines on Munch: Investigations of Water Damages on the Painting *The Source*

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Print: The University Print Centre, University of Oslo

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*"(...) we cannot claim to be fully satisfied with our present state of understanding of the material structure, and the deterioration over time, of any layer of a painting."*

*(J.H. Townsend, in Wolbers 2000:viii)*

**ABSTRACT**

This dissertation discusses issues related to a tide-line on one of Edvard Munch's large-scale paintings, *The Source,* in the Oslo University Assembly Hall, the Aula. The Aula paintings were produced in the period 1909-1916, executed in oil on primed canvas. Both paint and priming layers are thin and lean, and the paint surfaces have never been varnished. The main focus and question for the study has been whether the materials in the water damaged area of the painting might have been affected more than visually, and whether change might have occurred to the material composition in the area. It might be possible that, varying with the medium and pigment composition of the paint, water may have a profound impact on the paintings materials. It is likely that tide-lines on a medium-poor surface, as on *The Source,* are the result of particles transported by water. The study has therefore focused on analyses of particles in the tide-line area, in an attempt to determine possible alterations in the affected area.

The results from the analyses of the tide-line on *The Source* indicate that the content of some particles in the paint layers, like Zn, Al and Ca containing particles, varies between unaffected and affected areas of the painting, in terms of decreased or elevated levels of elements, thus demonstrating the effects of water on the painting materials. This may be related to the hygroscopic qualities of the pigments containing these elements (like zinc white and ultramarine) as well as to the fact that little binding medium binds and protects the particles from water. The reaction of painting materials to water might thus be both a chemical reaction, according to the hygroscopic properties of the present elements, and a more physical reaction where leanly bound particles are transported by the water. It is further suggested that broader analyses should be carried out to achieve a more in-depth understanding of the tide-line phenomenon in order to be able to make the right treatment decisions for these kinds of damages.

## INTRODUCTION

Tide-lines resulting from water damages are a frequent occurring problem on paintings, whether they have been poorly treated, hung in a poor environment or been subject to an accident. Tide-lines on painted materials have also been both treated and reported in different ways (Landro et al, 2008/ Solberg, 1997/ Daly Hartin et al, 1999/ Vuori et al, 2000). But the possible consequences of these damages to the painted surface - of what might actually have happened to the materials affected by the water and if they have been altered or moved in any way - have been subject to little or no thorough investigation.

In treating damages like tide-lines, conservators tend to focus on the visual aspects of the damage and the condition of the affected painting, often without a thorough understanding of the phenomena underlying the condition. Water might in such circumstances have brought different materials to the painted surface and/or affected the painting materials themselves, thereby also affecting the structure and composition of the materials. It might be possible that, varying with the medium and pigment composition of the paint, water makes a profound impact on the materials in the paint and possibly moves elements in and on the painted surface.

Systematic studies considering the characterization and investigation of tide-lines on visual art have been carried out, but primarily on cellulosic artefacts of paper or textiles. In the case of tide-lines on e.g. a paper artefact, the affected material will mainly be the cellulose of the paper. In paintings, however, there often is a broader range of materials that could be affected, considering the often complex structure of paint and ground on a support material of various kinds.

It has been the aim of this study to try to look at how paint layers might have been affected by water and dirt in a tide-line area, and thereby find out more of what might have

happened to the painting materials in water damaged areas of a painting. It has been looked for ways of finding out whether and to what degree the composition of painting materials in the affected area might have been changed and/or shifted in some way. The study has been limited in some respects, concerning available time and analytical possibilities. This has consequently led to certain limitations regarding achieved results. It is though hoped for that the results that have come out of the study can support a better understanding of the tide-line phenomenon in order to take the right treatment decisions for these kinds of damages.

### *Research material: phenomenon, context and questions*

The visual signature of water damage is mainly a more or less pronounced brown framing of the affected area (Hutchins, 1983:57). Different approaches to the definition of damage and change occurring in the affected material mainly give the same conclusions of visually disturbing lines resulting from a degradation of the material in addition to a gathering of surface dirt. The marks occur as the dirt and degradation products are carried and deposited by spreading water. Studies made of tide-lines resulting from water damage on paper indicate that these marks contain both degradation products as well as dirt transported with the water, potentially causing mould growth (Hutchins, 1983:59-60/ Dupont 1996:18). The lines are therefore in these circumstances signs of both degradation of the material, which the water has passed through, and of collected surface material that might cause further damage to the material in question (Pedersoli and Ligterink, 2001:133).

The tide-line phenomenon might also be compared to the so-called *coffee-ring effect*, where material suspended in the staining liquid is described as being carried along to the rim of the staining drop and accumulated there to form a line or ring (Vermant, 2011:286/ Yunker et al, 2011:308). Different kinds of marks on a surface in terms of dark lines or rings caused

by an influence of water might be described as *tide-lines* or *spots*. Here, the term *tide-line* is defined as lines/marks on the surface of a painting caused by a more or less prolonged influence of water on the materials of a painting, where the water has carried deposits on top of and through all the layers of the painting. Areas where water has affected the surface for a shorter period of time, for instance in areas where water-based front protections have been applied and removed, and where smaller cleaning-tests have been made, will not be treated as a part of this study.

### *Munch's Aula paintings*

The starting point for the study is tide-lines on a large scale painting by Edvard Munch in the Oslo University Assembly Hall, the Aula. The Munch Aula paintings were produced in the period 1909-1916, and have undergone several different treatments over the years (Frøysaker, 2007:246). Recently, the paintings have undergone thorough investigations and treatments in the *Munch Aula Paintings Project* (MAP), led by Tine Frøysaker at Conservation Studies (IAKH), University of Oslo. However, some problems related to the conservation of the paintings are still to be resolved, among them investigations and possible treatments of large tide-lines on some of the paintings, including *The Source* (c. 448 x 225 cm)[1]. A large dark edged tide-line on *The Source* frames a band that is c. 12 cm in width, and covers the entire height of the painting on its right-hand side.

The main focus and question for this study has been whether the paint layers in the water damaged area of the painting might have been affected more than only in a superficial, visual way, and whether a change might have occurred to the materials and material

[1] Woll no. 1226.

**Figure 1:** Edvard Munch's *The Source*. Full figure photo after re-installment in the Aula, after treatment in the *Munch Aula Paintings Project* (MAP) (Photo: Terje Heiestad / UiO, 2012. © The Munch Museum / The Munch-Ellingsen Group / BONO, Oslo 2014)

compositions present in the tide-line area. It is believed that this will be of significance when deciding how the damaged area of the painting should be treated.

As discussed by Tine Frøysaker in her reflections regarding the treatment of the Aula paintings during the MAP project, the decisions regarding treatment of the paintings cannot be based strictly on aesthetic considerations. Referring to the vulnerability of Munch's paintings, treatments like cleaning procedures can involve a risk of loss of original material. Munch's technique, using highly diluted colours on lean and absorbent grounds, has resulted in paint surfaces that easily can suffer from loss of paint fragments if mechanical cleaning is performed, as well as loss of migrating particles or leaching of soluble components if a solvent based cleaning is conducted (Frøysaker, 2007:254). The possible risks and benefits associated with treatment of surfaces like the ones presented by Edvard Munch's paintings therefore have to be balanced against each other, evaluated on the basis of thorough investigations.

*The paint*

The paint itself, being the upper most and foremost layers of a painting, will consequently be the most vulnerable part of the painting. But at the same time these layers will be some of the most important and signifying parts of the painting as they are reflecting the "imprints" of the different processes the painting has undergone (Hedley et al, 1993:103). Correspondingly, it is in the surface of the painting we find the most pronounced effects of a tide-line, in terms of gathering of dirt and degradation products as well as possible alterations of the surface materials.

**Figure 2:** Detail photo of tide-line on *The Source.* Rim of tide-line appearing as brown lines. (Photo: K- Scharffenberg, 2010)

It can be difficult to understand fully and get hold of what might actually have happened to the painting's surface materials in a tide-line area, but by looking at the different material aspects of a paint layer it can be possible to get hold of and understand at least some parts of the full picture of this kind of damage. As this study has focused on tide-lines on a painting by Edvard Munch, it will be relevant to have a closer look at both the painting materials of the specific painting in particular and of Edvard Munch's paintings in general.

Also a broader look at characteristics of paints related to Munch's paintings will be of significance to this study.

The Aula paintings are executed in oil on primed canvas, and like so many of Edvard Munch's paintings, the paint and priming layers of the Aula Paintings are thin and lean, with surfaces that never have been varnished. It is thus easy to imagine the sensitivity of these paint surfaces, particularly when exposed to moisture.

A variety of factors may play a role in how a paint layer will react when exposed to water and moisture, as the paint properties will vary both according to the composition and the age of the paint. Medium poor, lean and dry paint surfaces, like the ones seen in Munch's Aula paintings, will be particularly susceptible to moisture, with no surface coating and little hydrophobic medium surrounding and protecting the pigment particles from the influence of the water. Also the properties of the binding medium and the different pigments in the paint, as well as the age of the paint layer, will have influence on the paint layer's behavior when affected by water. Looking at paints' stability after exposure to high moisture levels, Marion Mecklenburg stated that the properties and stability of dry paint films will vary with the pigment and the medium content of the paint, and thus the reactions of the different paint layers of the painting will vary (Mecklenburg, 2007:24). Likewise, the age of a paint layer will be of importance to its resistance towards water, as the ageing processes of drying paints will make the paint layers more or less hydrophobic/hydrophilic, according to both medium and pigment content.

An understanding of the character and build-up of the affected paint layers in a tide-line will in this respect be essential when trying to understand what reactions might have taken place in the damaged area.

*The water*

Water-induced tide-lines on paintings with lean, medium-poor surfaces, like Edvard Munch's paintings, will in all likelihood be the result of water that has transported particles of fine dirt and/or pigment particles (M. Mecklenburg, personal correspondence, 6th May 2011). The painting can in some ways be seen as a chromatogram, and the pattern of a tide-line can be compared to the pattern of separated substances obtained by chromatography, depicting different paths of elements in and through the substrate material. The water will thus function as a chromatographic force, marking a tide-line pattern on the picture surface containing elements deposited at different stages on the surface.

In addition to marking its way on a paint surface as a carrier of particle material, the water will influence and possibly degrade the affected paint material in different ways. As the paint layers' different character and composition of materials will be crucial for its reaction towards water, this will also lead to a different absorption of moisture in the paint layers and thereby a greater or lesser degree of change as the moisture is absorbed and eventually evaporated. In comparing different organic solvents with water concerning the interaction with the paint surface, Hedley et al (1993) stated that water produced the greatest surface change in different paint qualities, both applied through immersion and by swab-rolling (Hedley et al, 1993:105). Water and moisture are described as plasticizers and their removal results in stiffer films with higher softening temperatures (Hedley et al, 1993:107). The water will thus be able to change both the inherent character of the paint as well as the build-up and composition of the affected areas of the paint layer.

### *Dissertation structure*

This dissertation looks at different aspects connected to the problem of tide-lines, specifically those concerning the investigations of a tide-line on Edvard Munch's *The Source*. The study will firstly try to put the posed questions in to a context of previous studies on related material, both concerning earlier studies on tide-line questions as well as studies on related painting materials and degradation problems connected to these. Also earlier investigations on water and water's effect on unvarnished oil paint will addressed. Earlier studies on relevant methods for analysis will be taken into account before presenting the research methods for this study, including research question and collection of data. The relevance and use, including benefits and drawbacks, of selected methods for analysis will be given a closer look in order to support the choices made concerning selection of analytical methods and procedures.

Achieved results will be considered, both intellectual and analytical results. The issue of tide-lines on Munch materials will be treated in the light of a physical and intellectual context where registrations of Munch's materials and methods, as well as the long-term behaviour of the materials especially in association with aqueous influences. The analytical results, achieved via the chosen analytical methods, will be regarded as information supporting the more theoretical founded results. Data and interpretations of data will be presented as far as this has been achieved, within the limitations of time and available methods.

Final discussions summarize the research outcomes and applications of the study, especially regarding Munch paintings and related material. Considering the limitations that have dictated some of the choices for the study, several options for further research have been suggested. The present study should be seen as a starting point for a range of possible and relevant studies and investigations regarding tide-lines and their impact on painted materials.

## EARLIER STUDIES: MUNCH AND TIDE LINES IN CONTEXT

Few studies on the effects and treatments of tide-lines on paintings have been undertaken, and their focus has mainly been on the elimination of the visually disturbing effects of the lines, rather than examination of the damage itself. The majority of earlier studies on tide-lines is connected to damages on paper and textiles, where no paint or ground layers are present. A few investigations have been undertaken on painted materials as well, but these seem to be based on a similar approach to the issue as for the cellulosic material, that is with a major concern for the elimination of their visually disturbing effect.

A survey of the more comprehensive investigations and treatments of tide-lines on paper and textiles will be a natural starting point and reference in the study of tide-lines on paintings, together with a look at studies made of tide-lines occurring on painted surfaces. This does not, however, imply that the studies and treatments of the different materials, whether paper, textile or painted material, are seen as directly transferable. They will serve as framework for achieving a better understanding of the studied material.

For this dissertation, it has been looked at earlier studies of Munch's materials related to the materials present in the painting *The Source,* as well as studies of related painting materials in general and water's effect on these materials. These studies are relevant for the understanding of processes that have taken place in the area of the tide-line damage. Earlier studies related to the use of water as a solvent, in connection with cleaning of unvarnished surfaces, are also relevant. These studies address issues concerning the reaction of painting materials to water and moist environments, being essential for the understanding of possible mechanisms taking place in the tide-line area.

In order to make choices that are as appropriate as possible regarding analytical methods for in depth studies of the material in question, earlier studies of analyses have been

reviewed, limited to XRF and SEM methods. While a complete survey of earlier studies has not been attempted, a selection of earlier studies highlights the themes connected to the relevant subjects treated in this study.

### *Definitions and investigations of tide-lines on cellulosic material*

Many studies have been conducted, beginning as it seems in the 1930s, on the characterization and investigation of water damages and tide-lines on visual art made of cellulosic materials like paper and textiles. The studies mainly concentrate on analyses regarding changes and processes occurring to the fibrous, cellulosic material, and the earliest studies of water's impact on cellulosic material seems to be articles in Science and Technology Journals like *Journal of the Society of Dyers and Colourists* or *Nature* (e g articles by W.A. Bone and H.A. Turner). In their article 'Reactions at Wet-Dry Interfaces on Fibrous Materials', Schaeffer, Appel and Forziati (1955) focused on the reactions of cellulose in areas affected by water or other liquids, and the nature of the reactions. The described reactions are confined to chemical modification of either liquid or fibrous material at the wet-dry interface, and all reactions are characterized by the formation at the wet-dry interface of a brown line that fluoresces in ultraviolet light (Schaeffer et al, 1955:106).

The definition of tide-lines, or water stains, has likewise been given by Hutchins (1983) in his review of literature on water-stained cellulosics. He defined tide-lines as "a brown boundary that varies in intensity, width, brittleness, and permanence" (Hutchins, 1983:57), resulting from the water's carriage and deposition of dirt and degradation products from the affected materials. Hutchins defined the lines not only as a consequence of spread out and deposited dirt and decomposed cellulosic material, but also as sources of damage to cellulose as the boundary area is acidic as well as being a favourable environment to for

example the growth of *Aspergillus niger*[2] (Hutchins, 1983:58-59). However none of the earlier studies done on tide-lines connected to damages on paper and textiles seem to include concerns for or measurements of materials found in paint or ground layers. Thus it seems that a uniform understanding and view of problems connected to water damages has been adopted for damages on the often widely different surfaces comprising either paint layers or uncovered cellulosic materials.

Treatments of tide-lines on painted materials have been undertaken, and some definitions have been made also regarding these kinds of damages on painted surfaces. Among these are investigations and treatments of distempered panels (Solberg, 1997). In her treatment of distempered panels in Nore church, Solberg described the water-stains as dark lines gathered at the fringe of the wetted areas, containing materials that were transported by water, like dirt, concentrated glue (from the paint), pigments and water soluble materials from the wood. The stained, dark line is often shown to be harder, glossier and less soluble than the distemper (Solberg, 1997:18). Nonetheless, the use of an aqueous method for dissolving and moving of the aesthetically disturbing line was used for the treatment of the water damaged distemper (Solberg, 1997:20-21).

After the theft of the version of Munch's *Scream*[3] from the Oslo Munch Museum in 2004, and its return to the museum in 2006, the painting showed a substantial tide-line in its lower left corner (Landro et al, 2008:57). The damage was described as exhibiting a brown, yellowish fluorescing peripheral zone, formed as the damaging fluid spread out and brought with it material that was deposited in the paint structure. The rim of the tide-line was thus characterized as a gathering of water-soluble material, such as decomposition products (Landro et al, 2008:66). The dark colour of the rim emphasized the contrast between damaged and undamaged area, and a reduction of the dark line was highly desired both for conservation and for aesthetical reasons. As the tide-line was recognized as caused by water, the damage

[2] ***Aspergillus niger*** is a black filamentous ascomycete fungus, known to secrete a variety of hydrolytic enzymes capable of degrading plant biomass into sugars, among other characteristics (Tsang et al, 2009:153).
[3] Woll no. 896.

was seen as water treatable, based on the principle of "like dissolves like" (Landro et al, 2008:71).

The water-solubility of the tide-lines, both in their formation and their treatment, can serve as a guideline in the characterization and analysis of them. This seems also to have been a guiding factor for investigations of tide-lines on Munch's paintings. Many water damages have been found on Munch's paintings, and studies have been made of some of the damages, mainly directed by issues concerning treatment of affected areas. The water solubility of the tide-lines, combined with the concern for using water on porous substrates like Munch's paint surfaces, seem to have dictated the approach to and handling of the tide-lines. Aesthetic evaluations have been highly rated in treatments and investigations prior to treatments, both regarding the possible treatments of *Scream* and treatments of other paintings by Munch (Landro et al, 2008/ Sandbakken and Tveit, 2012).

### *Investigations on the Munch materials and degradation*

All together earlier registrations concerning Munch's painting materials will be significant for the interpretation and understanding of the different paint layers investigated in this study and the analyses performed on affected paint layers. Subsequently, earlier studies regarding both Munch's materials and techniques in general and the materials and techniques used on *The Source* in particular have been studied to provide the best basis for understanding the material aspects of the investigated water damaged areas.

As with many of Edvard Munch's paintings, *The Source* is executed in a thin and sketchy manner, using a lean, medium poor paint. Several areas of the painting have uncovered ground, exposed as a part of the composition. This is a quite common feature in

Munch's paintings, as he, according to Ludvig Ravensberg's descriptions in his diaries of 1910 (LR 536 (5.1.1910), the Munch Museum archives), wanted his paintings to have a fresco-like appearance, achieved as the paint soaked into the canvases (Sandbakken and Tveit, 2012:88). In their studies of Munch's monumental sketches, Sandbakken and Tveit recorded several different paint media or mixtures used to achieve surfaces looking like fresco painting, but also methods involving a heavy thinning of the paints using turpentine as well as adding chalk to some of his paints to yield matte, and subsequently porous, paint layers (Sandbakken and Tveit, 2012:89). The same conscious exploitation of lean and dry surfaces can also be seen in the Aula paintings, and is also described concerning earlier investigations of the Aula paintings and other paintings by Munch (Frøysaker, 2007/ Aslaksby, 2002).

Combined with the fact that the painting never has been varnished, the lean and dry character of the paint surface of *The Source* makes it likely that the paint will be especially vulnerable to external influences from for instance water and airborne pollutants. This situation will also be enhanced by some of Munch's pigment use, for instance his frequent use of zinc oxide in his paints. Zinc oxide is reported as a pigment that both raises the humidity sensitivity of the paint by its hygroscopic properties, as well as having other properties that often can cause less durable paints (Tumosa and Mecklenburg, 2013:61 / Tempest et al, 2013:110).

Considering the lean and dry character of the paints, as well as the crucial role of the pigment use for the behaviour of the paint layer, it has been regarded as most appropriate to first of all look at the elemental, particle composition and possible change in the investigated damaged area of *The Source.*

### *Investigations on water and water's effect on unvarnished oil paint*

At the same time as water causes the most frequently encountered damages to paintings, it is efficiently and successfully used both in the structural treatment and cleaning of paintings. As described by Green (1990), water and aqueous solutions are frequently used in the cleaning of paintings, also when unvarnished, water-sensitive paintings are treated (Green, 1990:52-53). Depending on the character of the paint, material composition and age, the paint film will react to a varying extent to moisture. According to Mecklenburg (2007), the most serious RH related damages to paintings occur with very high moisture levels, but the properties of dry paint films and their durability after exposure to high moisture levels will vary with the pigment and the medium content of the paint (Mecklenburg, 2007:24). Both reactions and permeability of the paints will thus depend on the material composition of the paint layer. Permeability in porous paint will naturally be higher than in solid paint, and thus porous paint will have a weak resistance against climatic influences. Likewise, the often porous surface of an unvarnished painting makes this especially susceptible towards capillary forces, and the enhancement of these forces in introducing water is thus described by Perry (1990) as causing a common problem in cleaning porous substrates with aqueous solutions since the risk of attaching the dirt more strongly to the substrate is increased (Perry, 1990:6). In the use of aqueous methods for cleaning of paintings, Wolbers (2000) described the water's interaction with the paint surface. Water interferes with the forces present in the particle/surface interaction where soil is adhered to a surface. One of the most common forces present in soil adhesion are the capillary forces, noticeably enhanced when moisture is included in the action, thus securing small soil particulates onto the surface (Wolbers, 2000:3-4).

The sensitivity to aqueous surface treatment of certain twentieth-century unvarnished oil paintings is also a well-known and well-documented phenomenon, occurring in works with various environmental and physical histories. Investigations of these water sensitive paint films have shown a significant characteristic of paint containing both magnesium carbonate and zinc oxide, which are found in Munch's paints (Silvester et al,

2014:38/Sandbakken and Tveit, 2012:93). After exposure to atmospheres rich in sulphur dioxide and at conditions of high RH, dry paint films have had the ability to form magnesium/zinc and sulphur containing salts, i.e. hygroscopic sulphurous crystalline compounds, at the surface of the paint (Silvester et al, 2014: 49). It is suggested that increased water sensitivity in the investigated paint films may be due to a combination of the formation of hygroscopic degradation products and to weakening of the paint film due to salt-induced disruption of the surface (Silvester et al, 2014:38). It is thus easy to recognize the sensitivity to water-based treatments of these highly exposed and reactive paint surfaces.

Despite the severe complications that can be associated with the use of water in cleaning sensitive surfaces, the use of aqueous methods for treatment of tide-lines is shown to be most frequently used for cellulosic materials, and also on a wide variety of other materials (Solberg, 1997; Landro et al, 2008; Daly Hartin et al, 1999). This applies also for the treatment of many painted surfaces, described by Solberg (1997), among others. Water seems to have been regarded as the most appropriate treatment medium for damages caused by water, based on an understanding of the principle of "like dissolves like" working as the best treatment strategy. Little or no thorough investigations and analyses have been undertaken on the underlying mechanisms of the damages, in order to achieve the best basis for deciding how to handle the damages.

### *Methods for analysis*

For analysis and description of inorganic elements of the affected, tide-line area of the painting, relevant available methods have been considered and information sought in earlier descriptions of the methods.

The study has relied on portable x-ray fluorescence (XRF) analyser and the scanning electron microscope with energy dispersive X-ray (SEM-EDX). These methods are described in detail by Glinsman (2005) and Stuart (2007), among others.

XRF can, without the removal of a sample, quickly provide a survey of the elements present in an object. The XRF technique makes use of an X-ray tube, producing a beam of high energy photons that excites the elements in the sample. Each element in a sample contains a unique set of energy levels, and will thus produce X-rays with unique sets of energies (Stuart, 2007:234). Glinsman (2005) describes the energies as emitted in the X-ray region, and as defined by the energy difference between the excited and ground states of an atom (Glinsman, 2005:4). Electron transitions in the atom thus produce energies that are characteristic of the elements present in the sample, detected and recorded as a series of peaks in a spectrum. As the XRF technique does not differentiate between the different layers of the paint, all elements present at a spot of the painting will be presented simultaneously.

A portable XRF instrument can aid in the identification of inorganic pigments of paints as many pigments can be characterized by the presence of one or two detectable elements (Stuart, 2007:240). Stuart (2007) described in this way XRF spectroscopy as a non-destructive technique for the measurements of the elemental composition of materials (Stuart, 2007: 234). The use of a portable instrument like the XRF available for this research is thus considered as most convenient for achieving a non-invasive survey and overview of what elements are present in the different areas of the tide-line on *The Source.*

The convenience of portable instruments like the XRF analyser have of course been weighed against their limited analytical performance, as for instance light elements hardly can be detected by an XRF analyser since the measurements generally must be done through air (Glinsman, 2005:5-6/ Mantler, 2000:7). The information gained by XRF is thus presented as most beneficial when the technique is used in conjunction with other techniques (Glinsman, 2005:16). In investigating the changes in and on the paint films, the importance of using complementary techniques is emphasized by various authors (Hedley et al, 1993/ Nyström-Larsson, 2005/ Rosi et al, 2009/ Rosi et al, 2010/ White and Roy, 1998/ Khandekar, 2003),

and the information gained by a very close surface scrutiny of an object often has to be supplemented with the information gained through analysing samples if more exact and comprehensive information about the object's structure and materials is to be achieved (Khandekar, 2003:52). When it comes to the investigation of tide-lines on paintings, these complementary techniques should comprise the possibility for gaining both qualitative and more quantitative measurements.

For achieving more exact measurements of the elements present and their amount at the different stages of the tide-line, it was considered most appropriate to combine the XRF analysis with sample analysis performed by SEM-EDX. The SEM microscope requires sampling and mounting of samples for analysis, thus being an invasive technique. SEM is described as an analysing technique where the image of an object is created using a beam of electrons rather than traditional visible light (Stuart, 2007:91). In SEM, the surface of a sample is studied, and detailed three-dimensional images can be produced (Stuart, 2007:91-92). Combined with energy dispersive X-ray spectroscopy, EDX, elemental analysis and identification of very small samples can be carried out (Stuart, 2007:92).

The combined use of XRF and SEM-EDX techniques is demonstrated by O'Donoghue et al (2006) in the investigation of the 1938 Joan Miró painting *Groupe de Personnages* from the Los Angeles County Museum of Art. Non-destructive analysis was performed with a hand-held XRF analyser to elucidate the pigments in the ground and paint layers. In addition, cross-sections were prepared and examined with SEM-EDX, among other techniques, primarily in order to understand how the paint layers, including the ground, had been built up (O'Donoghue et al, 2006:64).

In addition to the use of SEM technique in detection of surface characteristics, the method can be used to investigate surface deposits. Uniformly distributed protrusions on the surface of the paint layers in later works (1934-1938) of the artist Alexej von Jawlensky were investigated by Zumbühl et al (2006) via cross-sections of the paint layers. By scanning electron microscopy backscattered electron and element mapping (SEM-BSE), Zumbühl et al localized agglomerations of zinc stearates in the upper part of the priming of the paintings.

Also in investigations performed on Edvard Munch's paintings, both XRF and SEM techniques has been used for identifications of pigments and particle composition of paints and grounds. In the investigations undertaken on the Munch Museum's version of *Scream*, both XRF and SEM techniques were used for analysis (Landro et al, 2008:73-74), and the use of SEM-EDX is described by Singer et al for analysis of several of Munch's paintings (Singer et al, 2010). In the MAP project, NITON's portable XRF instrument was used in situ for examinations and recordings of four of the Aula paintings (Frøysaker and Liu, 2009:46).

*The use of XRF and SEM methods for analysing materials on Munch paintings*

Both the use of XRF and SEM methods for analysing paintings materials is described in several articles regarding Munch's paintings and materials used in the paintings.

In the search of suitable treatment methods for the water damaged areas of the Munch Museum version of the painting *Scream,* sustained during the theft of the painting in 2004, the Museum conservators carried out several and in-depth studies of the area, including amongst others measurements and analyses performed with XRF and SEM (Landro et al, 2008:73-74). XRF measurements of the tide-line on *Scream* were performaed by Unn Plahter, registering a certain pattern of differences regarding the distribution of elements in water affected vs unaffected areas of the surface (Plahter, 2008).

Also in the analyses described by Singer et al, for investigations of several of Munch's paintings, SEM-EDX microscopy was used for the reading of elemental compositions of Munch's paints (Singer et al, 2010). A registration of elements in paint layers of the Aula paintings was also performed using a portable XRF instrument, gaining an indication of the total amount of elements in selected areas (Frøysaker and Liu, 2009: 46). As the XRF-spectrum is accumulative, it is difficult to distinguish the contents of the individual layers in a

multi-layered structure. The XRF measurements performed on the Aula paintings were therefore whenever possible done on single layer structures (Frøysaker and Liu, 2009: 47). Regarding measurements and sampling on *The Source*, this was done on as uniform and identical areas as possible to be able to compare water-affected and unaffected areas of the painting.

### *Non-destructive vs destructive and qualitative vs quantitative analysis for determination of material compositions*

As the X-rays from an XRF apparatus pass through all numerous layers of the analysed paint, and no dimensional information about the layers can be obtained, quantitative analysis will be difficult to achieve using XRF (Glinsman, 2005:7). As stated by Stuart and Glinsman, an XRF spectrum also has the disadvantage that it does not always provide unambiguous information regarding pigments, as many pigments may have the same elemental composition (Stuart, 2007:240/ Glinsman, 2005:9). But despite these and other drawbacks non-invasive techniques like the XRF measurements might show, the use of non-destructive analytical techniques for in situ application is often required as sampling may not be permissible or possible in a proper way (Lussier et al, 2007:46/ Scott et al, 2001:93/ Sciuti et al, 2001:132).

The damage done by sample taking when using a destructive technique like SEM is though, as mentioned earlier, often recognized as balanced by the information gained by analysing the sample (Khandekar, 2003:52). Thus, although electron microscopy all in all does have the drawback that it is a destructive technique, examinations of cross-sections by this technique can be instrumental in identifying, for example, pigment composition and surface characteristics of paintings. The versatility of a paint cross-section when analysed

with methods like SEM is enhanced by amongst others Khandekar (2003). The use of SEM technique in the investigation of paintings, materials and surface, will provide more quantitative, measurable data on the studied matter. Stuart describes the appropriate use of SEM in the studies of paintings for identifying inorganic pigment particles, and the use of EDS to distinguish pigments where they show similar appearances. Further, the surface characteristics of paintings may be investigated using scattered and back-scattered electron imaging in SEM (Stuart, 2007:95).

## RESEARCH METHODS

The choice of methods for investigating the material condition of the damaged area of *The Source* have been dictated by the character of the painting, the character of the damage, and by comparisons made with earlier studies on similar issues. Additionally, the initial attitude towards the performance of analysis was to do as much non-destructive analysis as possible. Sampling was only performed for the purpose of supplementing the non-destructive analysis with more quantitatively measurable analysis.

### *Questions and method*

The main focus and question for this research has been to try to determine how alterations from water and dirt in a water tide-line have affected the materials in an unvarnished painting like Edvard Munch's *The Source.* The starting point was the assumption that changes might have occurred in the painting materials, both in terms of displaced and added materials on the surface and in terms of degradation of the materials. In addition, the tide-line causes a visual distortion of the painting. It is assumed that both the painting's character as well as how the water ran over and through the paint structure will be of importance for how the painting has been affected. Especially on unvarnished paintings, painted with lean paints with low medium content, it is likely that water will have caused far greater distortions than in a painting painted with medium rich paints, covered with a layer of varnish. And, dependent on which pigments were used and what particles are present in the water, the painting materials will

presumably have been affected by the water in different ways. The study therefore focuses on a description of the build-up and composition of the paint layers as well as a characterization of how the water may have affected the paint in the area of the tide-line. Finally, attempts have been made to clarify what might have occurred of possible displacement and addition of particles in the affected area.

As the investigated painting is unvarnished and medium poor, the analysis of the paint structure will first of all focus on the particles that are present in the water affected area, and also try to figure out the disposition of particles in the tide-line. Although the colouring of a tide-line probably will not be caused by inorganic particles alone, it will be useful to attempt to determine the particle build-up and possible displacement in the affected area of the tide-line.

In treating all kinds of damages on paintings, a crucial question to answer before deciding what to do and what methods and materials to use will be in considering the condition of the original materials. It will be of great importance to try to find out what kind of change might have occurred in the present painting materials, both in terms of displaced and added material on the surface and in terms of degradation of the materials, before deciding treatment possibilities and final treatment of a tide-line.

### *Collection of data*

Data have been collected both in terms of intellectual, contextual material, including earlier studies on both interaction of paint and water in general and on Munch's paint. The purpose for the collection of analytical data, gained by XRF measurements and SEM-EDX analyses of samples, was to be able to support the readings of intellectual contexts by more measurable,

quantitative material. In addition, UV examination of the tide-line and surface investigation using a Dino Lite hand-held microscope was performed to achieve a fuller first-hand understanding of the affected area.

Measurements were performed and samples taken according to a defined pattern in order to make the resulting data as readable and comparative as possible (see mapping of points for measurements/sampling in figure 5, page 51). The investigated tide-line on *The Source* spans over the entire height of the picture, thus affecting in total six different colour zones. Measurements and sampling have been conducted in a repeated pattern outside, inside and in the border zone of the tide-line, summing up a total amount of 36 samples/measurement spots. The chosen spots were selected from areas that could be as comparable as possible. Measurements using a portable XRF and analyses of samples performed with SEM-EDX were chosen for mapping of particles and inorganic elements present in the area of the tide-line. The results gained from measurements and analyses will be looked at closer in a later section of the dissertation (see *The data: measurements and samples for analyses).*

***Methods and analyses***

Hand-held XRF apparatus and a SEM-EDX microscope were chosen for the definition of particles in the affected area and the attempt to determine a possible displacement of particles. In addition some analyses have been performed using FTIR and RAMAN microscopes in an attempt to achieve complementary information of the materials present in the tide-line. These analyses have though not been concluded, and will therefore not be included in this dissertation.

*XRF*

XRF-measurements were first of all performed to achieve an overall impression of what materials were present in the affected area and in rough, relative amounts at the different stages of the tide-line. As described earlier, XRF scanning can present the overall elemental signature of a measured area, though with some limitations connected to the lack of ability to separate different paint layers from each other as well as to record lighter elements.

The XRF measurements were performed using a Niton XL3t pXRF with GOLDD+ silicone drift detector, mining mode. The measurements were done in small spot mode, effectively a 3mm circular spot size.

*SEM-EDX*

SEM-EDX analyses were chosen for obtaining more exact measurements of the elements present and their amount at the different stages of the tide-line. Even if SEM-EDX is an invasive technique, where samples have to be taken out from the painting, the benefits of being able to receive more exact measurements were considered as outweighing these drawbacks. Because of the high magnifications obtained by electron microscopy, only very small samples are required, which means that precious samples may be studied without causing considerable damage.

The SEM-EDX analyses were performed using a Jeol JSM-84 scanning electron microscope with tungsten filament, EDX: Oxford Instruments model 6506 X-Ray detector

with INCA software, Secondary Electron imaging (SEI) and backscattered Electron imaging (SEI) modes. The instrument was operated at an accelerating voltage of 20kV.

### *Organization and presentation*

With the total maximum amount of 36 measurements/samples, the amount of collected data in the study has been manageable. At the same time, the study includes at least two different analytical methods with different/complementary results. It is therefore most appropriate to use a data organizing tool which gives a good picture of the results of the different analyses/measurements. It is also relevant to systemize all collected data to aid both the present and future work on the subject.

For this study, the analyses and measurements carried out for the different spots are most interesting when seen in comparison with each other. It is therefore appropriate to organize the collected data in a way that exposes as much comparable material as possible simultaneously. Of possible models, the best option for this study seems to be the cumulative table. Examples of these can for instance be seen in the comprehensive work describing and listing the features of the Norwegian medieval altar frontals, where Unn Plahter mainly used the table-form to present the registrations and results of her investigations (Plahter, 2004:23-32). In the same way, Plahter's XRF readings of the tide-line on Edvard Munch's *Scream* from the Munch Museum are listed in tables, with values related to a 0-value of untouched/undamaged area (Plahter, 2008). The use of table presentations can also be seen in the handling and presentation of the investigations and data gained in the work of the Aula project. An example of this can for instance be seen in the presentations of 88 cleaning tests performed and evaluated on the painting *The Chemistry*, with the aim of proposing a method to assess the cleaning system for the Aula paintings (Frøysaker et al, 2011:55-57).

In addition, graph presentations will also be used in presenting both XRF and SEM-EDX measurements, in an attempt to visualize the relative amounts of the different elements that has been measured.

Tables has been used to present the measurements from each selected spot of the paint surface separately, while graphs are used to compare the measurements of all spots from the same paint area with each other. The tables are thus used for the more cumulative listing of analytical results, whereas the graph presentations have been used for presenting a resume and comparison of the different results – see examples presented below in table 1 and graph 1. As neither the XRF nor the SEM-EDX analyses can be regarded as gaining fully quantitative results, tables and graphs will in this respect be used mainly to give a resume and comparison of the different results: the graphs presenting values described as small, medium or high concentrations of the registered elements.

Further examples where the tables and graphs have been used for organizing and presenting the achieved results are presented in a later section of the dissertation, concerning results (see: *The data: measurements and samples for analyses*).

*Examples of tables and graphs used for organization and presentation of results*

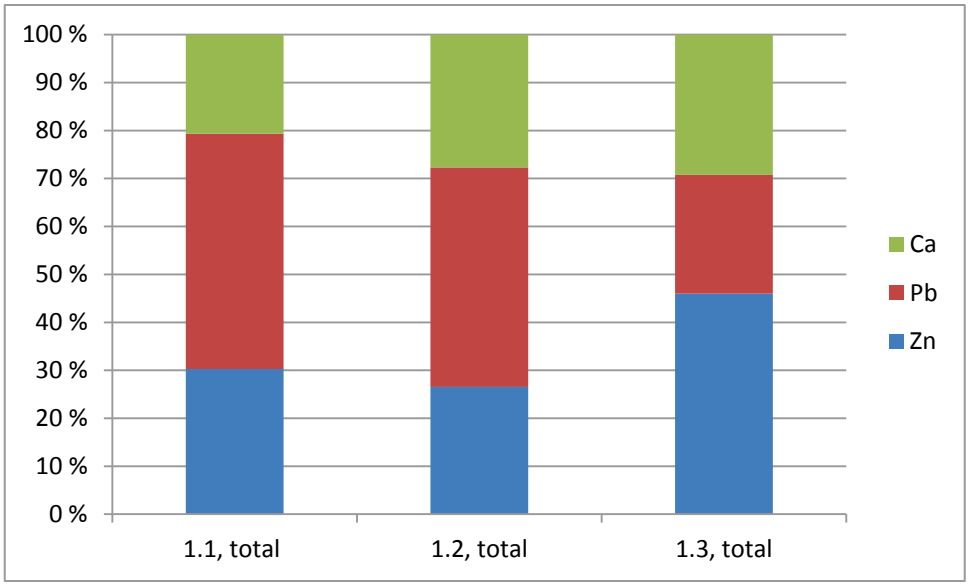
**Table 1:**

**SEM-EDX results from samples 1.1, 1.2 and 1.3 (transect no 1: light blue, sky area - measurements in atom%)**

| Sample from point per transect | Zn | Pb | Ca |
|---|---|---|---|
| **1.1** | 0,81 | 1,07 | 0,61 |
| **1.2** | 1,6 | 0,56 | 1,04 |
| **1.3** | 1,32 | 0,71 | 0,84 |

**Graph 1:**

**SEM-EDX results from samples 1.1, 1.2 and 1.3 (transect no 1: light blue, sky area - measurements in atom%) presented in graphs, for better visual comparison**



The overall picture given by the synthesis of the two presentations can give an impression of how the situation concerning the painting materials is in the investigated and presented area. Thus, the examples presented above seem to indicate that some main elements are present in different amounts at different stages of the investigated area of the picture – the content of some of the main elements seems to vary to some degree outside, inside and in the border-zone of the tide-line. An overall presentation and interpretation of all undertaken measurements and analyses are given in the later chapters on ‘Results’ and ‘Discussion’.

## TIDE-LINES ON MUNCH: PHYSICAL AND INTELLECTUAL CONTEXT

Dark tide-line marks are found on many paintings by Edvard Munch, in various degrees and to various extents. In 2005, a registration of the condition of the Munch Museum Collection stated that as many as 140 of the Museum's paintings have water stains or tide-lines of some kind (Stein, 2005:14). In her studies of Edvard Munch's unmounted sketches in the Munch Museum, Eva Tveit summed up the condition of the sketches and showed that of 41 paintings, 15 have large or many stains and tide-lines, 10 have medium amounts of stains/tide-lines and 13 have small amounts of stains/tide-lines (Tveit, 2011:134-135). This gives an indication of the amount of material with issues related to the findings of the study of tide-lines and their implications on painting materials.

While a few of the Munch Museum's paintings have been treated to diminish the visual distortions of the paintings' expression caused by the tide-lines (Stein, 2010), most of the paintings have been left untreated. As signs of different kinds of weathering have been interpreted as "authentic" artist-made features on the Munch paintings, most distortions and marks caused by some kind of weathering have been left intact. Another reason for leaving marks like water damages untreated has also been a lack of satisfactory approaches and methods for implementation of the treatments. After the theft of the version of Munch's *Scream* from the Oslo Munch Museum in 2004, and its return to the museum in 2006, the painting had suffered some damage including the occurrence of a tide-line in its lower left corner (Landro et al, 2008:57). Different aspects of the tide-line and related material in the painting were investigated using different methods, but the investigations on the altered painting materials were not conclusive. The Munch museum's conservators therefore concluded their investigations by leaving the tide-line untreated (Landro et al, 2008:58, 65, 72).

### *Munch's Aula paintings*

Some of the eleven large scale Munch paintings displayed in the Oslo University's Aula also show signs of water damage in form of tide-lines. During the last restoration of the Aula building, in the MAP project, huge areas of the building's ceiling showed signs of re-occurring flows of polluted water, which in many cases had reached and soiled the paintings too. Among the eleven paintings in the Aula hall at least three, being *The Source, The Sun* and *History,* show varying sizes of visible tide-lines. The tide-line on *The Source* seems to be the most pronounced one of these damages on the Aula paintings, as it covers the total height of the right side of the painting. This painting's damage is located just below profound water injuries in the ceiling (reported by architect J. Treider), and it is therefore obvious that this particular tide-line area is connected to conditions in the Aula, occurring during the painting's period in the Aula, and not to the artist's own doing.

Partly for this reason, the tide-line on *The Source* has been chosen for as subject for this study, as the question and discussion of whether the water damages are a part of an artistic intention or not, associated with Munch's own treatment of them, is avoided. The fact that the tide-line on *The Source* so easily can be connected to water leakages on the Aula's roof also makes it certain that the damage is caused by water and water transported materials. This will be normative for the approach to and selection of analysing methods and investigations of the tide-line areas, in the search for suitable methods for analysing possible changes to the painting materials in the affected area.

*Earlier studies and treatment history of* The Source

To achieve the best possible foundation for the interpretation of the investigations and analyses of the tide-line area in *The Source,* an overview of possible materials used in the painting was made on the basis of earlier registrations of materials used on Munch's paintings, particularly on the Aula paintings.

The eleven large scale paintings in the Oslo University's Aula were produced over a period of seven years, between 1909 and 1916, and are today Munch's only program of wall decoration that is still preserved *in situ* (Frøysaker, 2007:246). In total, the eleven Aula paintings cover c. 223 square meters, all paintings being of the same height, situated at the same level on the walls, but spanning over a variety of widths (Frøysaker, 2007:247). The paintings are executed on canvas, probably linen and, according to Munch himself, the most expensive canvas available from Holland (Frøysaker, 2007:248). Some of the paintings' canvas supports are formed of two or three pieces, and all in all the paintings comprise 18 individual pieces of canvas cut from eight different textiles (Frøysaker, 2007:248). Some of the canvas weaves are fine while others are coarse, resulting in a surface texture on the paintings which varies throughout the room (Frøysaker 2007:248). Before painting, the canvases were prepared with a ground that has been left uncovered and exposed in large areas on several of the finished paintings. Up to seven different grounds have been observed, based on either a glue and/or oil base, exhibiting surfaces varying from dry, thin to fatter, thicker ones (Frøysaker, 2007:248-9). Despite their relative difference, the general impression of the nature of most of the grounds is that they are quite lean and absorbent, adding an overall dry character to the paintings.

In 1926, the Aula paintings received a layer of white priming at their reverse side, showing in some areas on the front of the paintings as white drops as the priming occasionally have penetrated through the canvas weave (Frøysaker and Liu, 2009:48). In all likelihood the restorers applied the backside coating in an attempt to stop penetration of dirt from the brick

wall behind the paintings (Frøysaker et al, 2013). Munch himself also described the coating as a kind of "insulation" of the backside (Frøysaker, 2008:8).

**Figure 3:** Visible white spots of the ZnO containing backside coating which has penetrated through the canvas weave of the painting *Harvesting Women* (Woll 1228) (DinoLite photo by Karen Mengshoel, December 2010).

The original mountings and attachments to the wall for all the Aula paintings are today lost, due to a rescue campaign during the Second World War when almost all paintings were cut down in haste to be stored safely outside of the Aula hall (Frøysaker, 2007:250). When the paintings were reinstalled in the Aula, during the summer in 1946, they were glued onto a solid support of c. 6mm thick Masonite sheets, using rye flour paste (Frøysaker, 2007:250). The Masonite backings were in turn fixed to a wooden framework, anchored to the brick wall

of the building. During the last treatment of the paintings, undertaken between 2009 and 2011 in the MAP project, the wooden frameworks on the back of the paintings were removed and replaced by rigid honeycomb panels.

The treatment history of the Aula paintings include not only comprehensive structural interventions but also frequent cleaning campaigns, starting already in 1926, only ten years after their completion (Frøysaker, 2007:249-252). Between the paintings' installation in the Aula in 1916 the latest undertaken treatment of the paintings during the MAP project up to six cleaning campaigns have been registered (Frøysaker et al, 2011:53)

*Analyses*

To achieve the best support for the choice of cleaning methods used during the MAP project, thorough investigations were undertaken to form a basis for identifying pigments/elements that could be expected in the different paint layers and ground of the paintings, including *The Source* (Frøysaker & Liu, 2009/ Kempton, 2010). By comparing visual appearance of each colour with spectra obtained by a portable X-ray fluorescence instrument (XRF), the components of some of the materials used in the surface layers of *The Source* have been suggested (Frøysaker and Liu, 2009:47). The XRF measurements were done while the paintings still were mounted on the wall in the Aula, allowing only for measurements of the paint layers on the lower half of the painting. These will be considered below, in the description of the possible pigments used for the Aula paintings.

*Ground*

The ground in the painting is clearly visible in large areas, showing a rather thin, sparse layer leaving the texture of the canvas weave distinct. The ground is matte, lean and very absorbent, and both FTIR and XRF-examinations from the ground indicate zinc, lead and chalk (Kempton, 2010/Frøysaker and Liu, 2009:49). Regarding the binding medium of the ground used on the Aula paintings, this is suggested to be mainly glue, due to its matte and dry character (Frøysaker, 2007:248). FTIR analysis made of the ground of some of the paintings also showed contents of glue as well as traces of oil (Kempton, 2010). The oil content could possibly originate from the paint layers, absorbed by the dry ground

*Paint*

For the paint layers above the ground, visual examination indicates that a drying oil was used as binding media. This is also confirmed by FTIR analysis made of a few paint samples from the Aula paintings (performed by professor U. Plahter, University of Oslo, 2006), indicating a drying oil as binder for the paints (Frøysaker, 2008:6-7). The surface characteristics of *The Source* bear no signs of other materials than oil colours. Also Munch's own notes support this assertion, as he stated that he used oil colours for easel painting from Winsor and Newton when he executed his Aula paintings (Frøysaker and Liu, 2009:56).[4]

[4] Ongoing studies and analyses on Edvard Munch's surviving paint tubes (the Munch Museum) are performed by Dr. Hartmut Kutzke, University of Oslo, and paintings conservator PhD Biljana Topalova-Casadiego, the Munch Museum, Oslo.

The examinations undertaken of the Aula paintings suggest that Munch used the same support, ground and paintings technique without varnish for all of the paintings (Frøysaker et al, 2011:54). Most of the colours were applied in single layers on the bare ground, a few as transparent and the majority as semi-transparent or opaque layers (Frøysaker and Liu, 2009:53). Some colours were diluted, probably with turpentine, and applied as thin, fluid paints, while others have been applied as semi-solid or solid strokes, showing a range of impasto from low to high (Frøysaker and Liu, 2009:54). Allegedly, Munch mentioned his usage of turpentine with no explanation beyond calling it in his "own distinctive manner" (Frøysaker and Liu, 2009:56). Also in the sketches for the Aula paintings, a deliberate use of matte painting materials as well as a heavy thinning of the paints using turpentine has been reported (Sandbakken and Tveit, 2012:88-89). As the paint soaked into the canvases, Munch achieved a wanted fresco-like appearance, and also by adding chalk to some of his paints he achieved matte and porous paint layers.

The XRF examinations performed on the Aula paintings indicate that most of the colours consist of more than one pigment (Frøysaker and Liu, 2009:54). The violet colours (contours, shadows and middle tones in flesh colours, as well as tones in rock and water below and behind figures) of *The Source* contain cobalt blue combined with vermilion, and cobalt blue combined with both vermilion and a copper-containing pigment. The blue colours (different shades in water) display mixtures of ultramarine and cobalt blue, as well as a mixture of cobalt blue and zinc white (light blue). In addition a blue colour that includes Emerald or Scheele's green is seemingly mixed with Cerulean blue (dark water between the figures). Emerald or Scheele's green was also found among the green colours (in rendering of contours, hair and backgrounds of the figures) in *The Source*, as well as a green earth pigment, both appearing as single green pigments. For the yellows (contours and hair of figures), mixtures of cadmium yellow and vermilion seem to have been used, and for the reds (contours, middle tones and shadows in flesh colours of figures, as well as contour and shadow on rock behind seated figure) these contain vermilion and mixtures of vermilion and red ochre. Also mixtures of vermilion and a cobalt pigment are found in some of the red mixtures (middle tones in flesh colour and contour/shadow on rock), suggesting one

combination of vermilion, cobalt blue and maybe manganese violet and another combination of cobalt phosphate and/or organic red together with vermilion. The brownish red colours (shadows in flesh colour of seated figure) in *The Source* seem to be made up of a mixture of chrome green, an earth pigment, cadmium yellow and vermilion, while the browns (contour on rock below seated figure) appear to consist of a mixture of vermilion and an earth pigment. Finally, lead white and zinc white are the only white pigments suggested for the white and light shades of mixed white applications above the ground (highlights in flesh colours, waterfall and highlights in sky and water) (Frøysaker and Liu, 2009:54-55).

Analyses undertaken for this study of the paint layers affected by the tide-line in *The Source* also showed a corresponding set of elements present in the different paints. Besides the content of zinc (Zn), lead (Pb) and calcium (Ca), which all the paint layers seem to possess, the light blue colour (sky) showed a content of silicon (Si) and sulphur (S); the blue colour (mountain) a content of copper (Cu), cobalt (Co), barium (Ba), Si, S and aluminium (Al); the green (landscape) a content of Cu, arsenic (As), chrome (Cr), potassium (K), and S; the light red (flesh) a content of Cu and As; the white/ground layer a content of Cu and Co; and the light purple (water) an additional content of Cu.

The study conducted by Sandbakken and Tveit on Munch's sketches showed also here the use of an array of pigments, such as synthetic ultramarine, Prussian blue, cobalt blue, zinc oxide, lead white, chrome yellow, yellow ochre, vermillion, Scheele or emerald green and green zinc chromate (Sandbakken and Tveit, 2012:89). In the more overall study of different Munch paintings and sketches described by Singer et al, 22 different pigments and six different extenders or pigments usually associated with grounds were found. It was also found that the artist used a mixture of media, including drying oils (linseed or poppy seed), beeswax, egg and casein (Singer et al, 2010:287).

By exploiting a range of different pigments and paint medias, as well as methods for applying the paints on the canvas substrate, Munch could achieve just the light, dry, fresco-like appearance he wanted.

### *Kill or cure*

Marks of wear and weathering and degradation on Munch's paintings, such as tide-lines and even bird excrement, and the treatment and elimination of these have often been subject for discussions, as Munch himself often treated his paintings roughly, hanging them outside exposed to the elements (Aslaksby, 2002:285 / Stein, (1)2011:100 and (2)2011:273). Munch referred to this treatment as a *Kill or Cure* treatment, or "*Horse Cure" ("Hestekur"),* and it has been looked upon as reflecting a kind of artistic intention, leaving his paintings softened and lightened by the weathering (Aslaksby, 2002:285-287). By both painting in a thin and lean manner, as well as treating his paintings with a certain roughness, Munch could give his paintings the intended expression of a lightly tuned, fresco-like surface. Munch's frequent use of outdoor settings especially when working with large landscapes and figure compositions could both be a preference due to space requirements but also to achieve the desired effect of softened colours caused by the heavy exposure of the paintings to the elements (Aslaksby, 2002:285). The use of dilute oil paint and lean priming, accompanied by an unvarnished surface, was likewise a means to achieve a light and soft tonality (Aslaksby, 2002:287).

By reading traces of weathering and outdoor exposure on Munch's paintings as a part of his artistic intention and expression, they might themselves be subject for preservation and conservation, even if they potentially can cause further degradation of the paintings' materials. While this topic is of interest, the discussion of whether or not a tide-line should be preserved need not be addressed here as the study focuses on tide-lines ascribed to the paintings' period in the Aula. Questions regarding treatment of the tide-lines are in this case best seen in the light of an incomplete understanding of the material aspects of the damaged area.

Despite the probability that Munch in many cases gave his paintings a wanted "patination" through outdoors weathering, it is unlikely that an artist wants his paintings to become obscured by dirt and inherent changes in the materials due to damages and poor display conditions (Perry, 1990:4). It is therefore necessary to try to identify the material aspects of the tide-line area, to the extent that this is possible with the available instrumentation, to assess the presence of unwanted alterations of the paint materials.

### *Ageing and deterioration of the painting materials*

The process of drying and ageing of oils is a complex process that has been the topic of extensive research in Europe and the US.[5] Although these processes will not be addressed in detail here, the main characteristics will be described, relative to *The Source,* as well as the impact of different pigments on both the drying process and the final characteristics of the dried paint film.

Drying oils, being natural products, are multicomponent mixtures with a complex chemical composition, undergoing complex changes over time mainly because of ongoing degradation processes like oxidation, polymerization and hydrolysis (Spyros and Anglos, 2004:4929). The early stages of paint ageing are dominated by both autoxidation and hydrolysis, while mainly hydrolysis determines the long-term behaviour of the paint (Tumosa and Mecklenburg, 2013:51). Oils are, in short, described as esters of carboxylic acids, mainly unsaturated acids like oleic, linoleic and linolenic acids for the drying oils used for paints. Unsaturated bonds in the esters will, via an oxidation process where oxygen from the air is

[5] Examples of this can be seen in the work by for instance Keune, van den Berg, Mills and White, van der Weerd, van Loon and Boon (Keune, 2005/ van den Berg, 2001/ Mills and White, 1994/ van der Weerd, van Loon and Boon, 2005)

taken up, cross-link and polymerize to form a tangled three-dimensional network of bonds. However, the ester bonds may be easily hydrolysed during and after the polymerization reaction, and thereby release free fatty acids (Tumosa and Mecklenburg, 2013:51). The free fatty acids, as well as other oxidation products that appear as small molecules, will over time diffuse out of the oil film and result in a weight loss of the paint film. The weight loss might in turn produce voids within the film, and thereby a more vulnerable paint film (Tumosa and Mecklenburg, 2013:52). Thus, the loss of the low molecular weight compounds might "embrittle a paint film and promote cracking as well as loss of colour saturation" (Tumosa and Mecklenburg, 2013:57). This ageing process of an oil paint film means that it will, also as a result of natural processes, decompose and degrade to a certain extent, and become weaker, leaner and less bound.

In terms of Munch's paintings, this means that his paints, which initially were pigment heavy and porous, have become even more vulnerable over time, as well as more hydrophilic, caused by the hydrolysis process of the oil. Furthermore, the paint film in Munch's paintings is increasingly susceptible and vulnerable to influences from water, and an area of the painting where water has affected the paint layer will probably have undergone a heavier attack on an old painting than on a freshly painted surface.

Studies have shown that specific pigments in paints play a significant role in the ageing process of paint, as the pigments in paints are recognized as crucial and potentially reactive compounds in the paint (Van der Weerd et al, 2005:3). Certain metal ions, introduced for instance by the extraction of ions from the pigments in the paint, can enhance the initial autoxidation reaction of the oil, and thus affect the ultimate film formation and durability of oil paints (Tumosa and Mecklenburg, 2013:53). In terms of Munch's Aula paintings, there are certain pigments that can seem to be important for the character of the paint layers. These are mainly the zinc oxide white pigment, the earth pigments, the lead white pigment and what might be present of ultramarine. For instance, oil paints made with zinc oxide and cold-pressed linseed oil can become extremely brittle in a short time (Tumosa and Mecklenburg, 2013:61). This might also affect adjacent paint layers, making them less durable. In addition, earth pigments will lower the durability of paint layers, as these will enhance the hydrolysis

process in the paint. Conversely, a lead white paint can potentially increase the durability of all adjacent paint layers, as the lead white pigment will supply a so called “active” metal ion, catalysing the oxidation of the oil (Tumosa and Mecklenburg, 2013:65-66).

The effects of certain metal ions on the autoxidation of drying oils have been considerably investigated, and it has been shown that pigments can play several roles in the drying process of oils (van der Weerd et al, 2005 / Tempest et al, 2013). Likewise, paint’s different character, whether smooth, rough, close-packed or open, as well as their different content of pigments and medium proportions have been described as determining factors for their reaction towards and uptake of moisture (Hedley, 1993:120). The pigments in a paint layer are thus shown to be not only significant for the drying of paints, but also, as a result, for the water sensitivity of the paints (Tempest et al, 2013:109). Again zinc oxide pigment plays a central role, as this pigment’s hydrophilic character will result in a highly water sensitive paint. This also applies to the ultramarine pigment, and paints containing ultramarine.

As the ground layer on the *The Source* is shown to contain a considerable amount of zinc white, it can be expected that this might have affected the paint layers in total. It is likely that the presence of zinc oxide in the surface layers of the painting (some of which also might have migrated from the backside treatment of the canvas from 1926) will have made the layers more vulnerable and probably also more water sensitive. Enhanced by the leanness of the paint, painted on highly absorbing supports, the paint layers of *The Source* must be seen as especially delicate and vulnerable, both according to how they are applied but also according to their content of binding medium and pigments, including added zinc from the secondary backside treatment.

### *Water and dirt*

The influence of water and aqueous solutions on paint layers of different kinds has also been thoroughly studied and explained, especially in the literature discussing various methods for cleaning of paintings.[6] Based on these studies, it might be possible to evaluate how and to what degree the water that ran over the paint surface of *The Source* may have influenced both soil adhesion and transportation of particles of various kinds in the tide-line area. The studies of aqueous methods used for treatment of paintings can provide an understanding of water's physical and more chemical effects on the materials of a painting, as they can show how water may move and chemically alter the materials in question. Water may also influence both the deposition and attachment of dirt to a painted surface.

The deposition of dirt on painted surfaces is a process involving a complex interaction of many factors, mainly related to the external environment (e.g., dirt in the air, relative humidity and temperature), the dirt itself (chemical composition and size) and the nature of the paint, including chemistry and surface properties (Phenix and Burnstock, 1990: 11). Usually, the characteristics and properties of paint and varnish surfaces that can most often be cited as responsible for retaining soiling materials are: roughness, moisture resistance, elasticity, relative hydrophobicity and hydrophilicity, tackiness, and electrical properties (Wolbers, 2000:2). Unvarnished paintings, like the Aula paintings, will be especially vulnerable to the influence of water because they are relatively porous, making them more susceptible to capillary forces. In addition, the soiling material and its size will be a critical parameter in estimating the forces likely to develop and retain it on any given surface.

[6] Examples of this can for instance be seen in J.H. Stoner and R. Rushfield's book on "Conservation of Easel Paintings" (Routledge, 2013) and R. Wolbers' book on "Cleaning Painted Surfaces: Aqueous Methods" (Archetype Publications, 2000).

Soiling materials are often a mixture of particle types, and can exhibit a wide range of particle sizes. As a function of size, certain forces of adhesion tend to predominate over others between particles and surface (Wolbers, 2000:2). The enhancement of adhesion forces in introducing water can thus cause a common problem in cleaning porous substrates with aqueous solutions since the risk of attaching the dirt more strongly to the substrate is increased (Perry 1990: 6). One of the most common forces present in soil adhesion are the capillary forces, noticeably enhanced when moisture is included in the action, thus securing small soil particulates onto the surface (Wolbers, 2000:3-4). The soiling of paint is presented as an adhesive process, where the capillary forces, in the presence of a liquid, operates as a mechanism of adhesion. The forces of capillary action are, according to Phenix and Burnstock, dependent on particle size and surface roughness of the containing surfaces (Phenix and Burnstock, 1990:13). At very high relative humidity and relatively low particle radius, water can condense between particles and surface, and act as a direct (liquid) adhesive between surface and particle. Thus, the capillary forces tend to increase as particle size decreases (Wolbers, 2000:3). Like a chromatogram pattern of separated substances, the water will mark a tide-line pattern on the picture surface containing elements deposited at different stages on the surface. On *The Source* it can seem like both small dirt and pigment particles have been moved by the water and secured to the lean and dry, water absorbent paint and ground surface. The water has apparently carried the particles on its way in and through the paint substrate, and the particles seem to have been deposited in a pattern according to the water route.

In addition to the importance of the particle character for the dirt adhesion process, the character of the paint film will play an important role in this process, especially connected to how water will affect the surface. Generally, the more moisture permeable a film is, the more hygroscopic the surface, and the more easily water can be absorbed onto and even condense there affecting the types of forces possible to secure soil particulates. Conversely the more hydrophobic, or less water permeable a film is, the less significant role water will play in either disrupting electrical or coulombic forces, and as an adhesive by condensation (Wolbers, 2000:4) The hardness of paint and varnish films can also affect the type and magnitude of the

interaction contributing to the overall force of adhesion of a soil particulate. The number of contact points, as well as the force of adhesion, between particle and surface might be bigger on a roughened surface than on an absolutely smooth surface (Wolbers, 2000:3). As *The Source* can be seen as having a rather rough surface, with leanly bound and exposed particles, it can be easy to imagine that the paint surface will be predisposed for enhanced adhesion of dirt particles as well as increased capillary properties as water is introduced. The dry surface will have soaked the fluid, containing the dirt particles, and both dirt and dissolved pigment particles will have been moved with the fluid front in the voids between more substantial paint elements, and the particles will have been secured in the material web where the fluid front have stopped and the particles have been prevented from moving any further.

### *Metal soaps and oxalates*

In addition to dirt, other kinds of contaminating materials may affect the paint surface of unvarnished, exposed paint. In 2008, non-invasive measurements carried out by MOLAB[7] with mid-FTIR spectroscopy revealed that the Aula paintings are affected by surface materials like sulphates, silicates, metal soaps and zinc oxalates (Frøysaker et al, 2013: 121). Sulphates and silicates were identified on exposed areas as a grey dust layer, while the metal soaps (Pb/Zn) and zinc oxalates are still invisible to the naked eye.

It is relevant to look at the interaction between these surface components and the water in the tide-lines, as the development of at least some of the surface contaminants will be promoted by high relative humidity, among other factors (Frøysaker et al, 2013: 122). The

[7] MOLAB Transnational Access Service provides mobile facilities for in situ non-invasive measurements, and is a part of CHARISMA (Cultural Heritage Advanced Research Infrastructures – Synergy for a Multidisciplinary Approach to Conservation/Restoration).

consequences of treating and removing such contaminants is not yet known, and for this reason it was decided in the last treatment of the Aula paintings, during the MAP project, to choose a method for surface cleaning of the Aula paintings that did not remove the contaminants (dry cleaning with polyurethane sponges). In the same way, the appearance of the surface contaminants in the tide-line areas might affect the treatment possibilities of these areas. Although the deposited material from the water that has caused the tide-lines might be different, the study and evaluation of the Aula tide-lines will potentially have implications for evaluation and treatment of tide-lines on other paintings by Munch and his contemporaries.

## RESULTS

Results have been achieved both in terms of intellectual, contextual material as well as more analytical material. The analytically achieved results, derived from the chosen analytical methods, are interpreted in the light of the physical and intellectual context of knowledge regarding Munch's methods and materials, their long-term behaviour and reactions towards water and moisture.

Samples have been analysed and measurements taken from selected areas of the tide-line, and a resulting set of data is gathered and organized to compare affected and un-affected areas of the painting. The aim has been to present a more detailed picture of the material situation in the tide-line area.

### *The tide-line area*

*The Source* measures ca 4,5 x 2,25 m, and the tide-line, running from the top to the bottom of the right side of the painting, comprises about 0,45m² in total. The tide-line runs over different layers of paint and ground, emerging as an overall lighter band with dark edges on the paint surface.

The tide-line crosses mainly six different paint layers, as well as some areas of exposed ground. The affected paint layers are, from top to bottom of the painting, a light blue (sky), blue (mountain), green (landscape), light red (flesh), white/ground (heel) and light

purple (water). The character of the paint layers shifts from thick, opaque and bold ones to semi-transparent and transparent, more dry layers. The matte, dry and lean paint surfaces seem to dominate most of the surfaces, indicating porous and mainly pigment heavy paints. The oil in the paint has seemingly been modified to a greater or lesser extent by a diluent, making the layers more or less medium poor. This will in some areas have led to a greater exposure of the pigments and fillers in the surface of the paint. In the tide-line areas the exposed pigments are expected to include cobalt blue, ultramarine blue, Emerald or Scheele's green, vermilion red, lead white and zinc white.

The tide-line appears as a continuous lighter band with a somewhat matter surface than the surrounding areas. The brown edge on either side of the lighter band emerges as a condensed gathering of dirt and paint particles or elements which might have moved with the water front. It can thus be expected that water running over the paint surface would impoverish the paint and ground layers, by extracting both organic and inorganic components and moving them to the edge of the water's expansion area, making the paint layers even matter and more lean than they originally were.

### *Analytical results*

The fact that *The Source* has highly exposed particles makes it likely that the water might have affected the particle composition of the paint in some way. It has thus been useful to try to determine the composition of particles in the affected area of the tide-line. For this reason the study initially focused on analyses of the disposition of particles in the tide-line, in an attempt to determine the possible displacement and/or addition of particles in the affected area.

As the water that caused the tide-line both was added to and evaporated from the surface layers of the painting, analyses was directed first at detecting alterations of materials in the tide-lines on *The Source*. Resulting sets of data have been gathered and organized to compare affected and un-affected areas of the painting, to determine to the extent that particles have been moved, added, subtracted or changed at the different stages of the tide-line.

***The data: measurements and samples for analyses***

The tide-line area was examined first using UV illumination as well as Dino Lite hand-held microscope. UV photographs were taken of all the paint areas affected by the tide-line, while recordings using the Dino Lite microscope only were performed on certain spots of the tide-line.

As the tide-line on *The Source* spans the entire height of the picture, it affects several different paint surfaces. In total, the area affected by the line can be divided into 6 different main colour surfaces, transects, and XRF measurements were done on each of these. Each measurement was done in 4 ranges (30s per range):

| Range | Different modes (using different voltage (kV), current (μA) and filters to target different elements) | Voltage (kV) | Current (uA)* |
|---|---|---|---|
| Main | Mn – Bi (can see Ti, V, Cr and lighter elements but not as sensitive as low or light ranges) | 50 | Up to 40 |
| High | Ba to Ag, | 50 | Up to 40 |
| Low | K – Cr | 20 | Up to 100 |
| Light | Light element analysis (e,g, Mg-Cl) (consider He purge) | 8 | Up to 199 |

*Automatically selected by the analyser - higher dead time, lower current

For the affected colours, measurements were made repeatedly for areas outside the tide-line, in the border zones of the tide-line and in the middle of the tide-line. Thus the painting was analysed across a series of transects covering the tide-line, at different points according to the different areas. The transects and points were ordered as follows:

**Transects:**

| Number | Location |
|---|---|
| 1 | Light blue (sky) |
| 2 | Blue (mountain) |
| 3 | Green (landscape) |
| 4 | Light red (flesh) |
| 5 | White/ ground (heel) |
| 6 | Light purple (water) |

**Points per transect:**

| Number | Location |
|---|---|
| 1 | Left side outside tide mark |
| 2 | Border region to left of tide mark |
| 3 | Tide mark |
| 4 | Border region to right of tide mark |
| 5 | Right side outside the tide mark |

Each measurement thus has a two-ciphered number, with the number for the transect listed first and the number for the point per transect listed secondly (1.1, 1.2, 1.3 etc). By using this repeated pattern for the measurements, the amount of measurement spots counted 36 in total.

The same system was used when collecting samples for mapping and analysis with SEM-EDX, building up a sample collection representing both unaffected and affected areas associated with all transects of the tide-line area. The samples collected from transect no 5 (white/ground, heel of standing figure) turned out to be unsuitable for mounting for cross-sectioning, and are therefore saved for later analysis with for instance FTIR or Raman microscopes. After preparation of the other samples into cross sections, and examinations under ordinary light microscope, only a selection of the total amount of samples were chosen for analysing in SEM microscope. The selection was done according to what was considered realizable and feasible within available time and resources. Additionally, the results gained from analyses of the selected cross sections were considered to give a representative, first-hand picture concerning the parts of the tide-line that were deemed important to examine. The analyses that were done in the SEM microscope were conducted both as mappings across the entire sample, comprising all layers of the sample, as well as spot measurements of selected

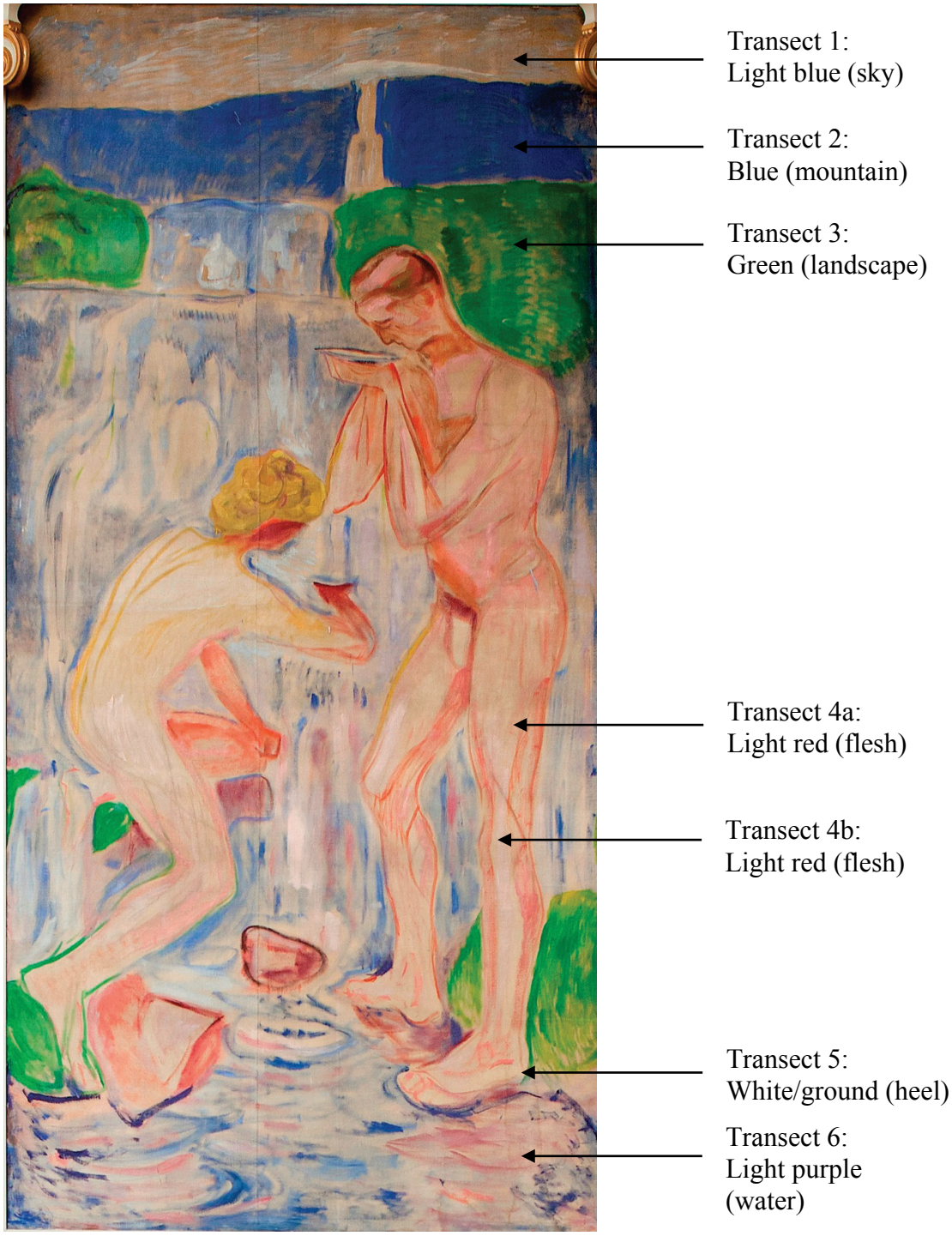



**Figure 4:** Transect areas for measurements/samling (Photo: Terje Heiestad / UiO, 2012. © The Munch Museum / The Munch-Ellingsen Group / BONO, Oslo 2014)

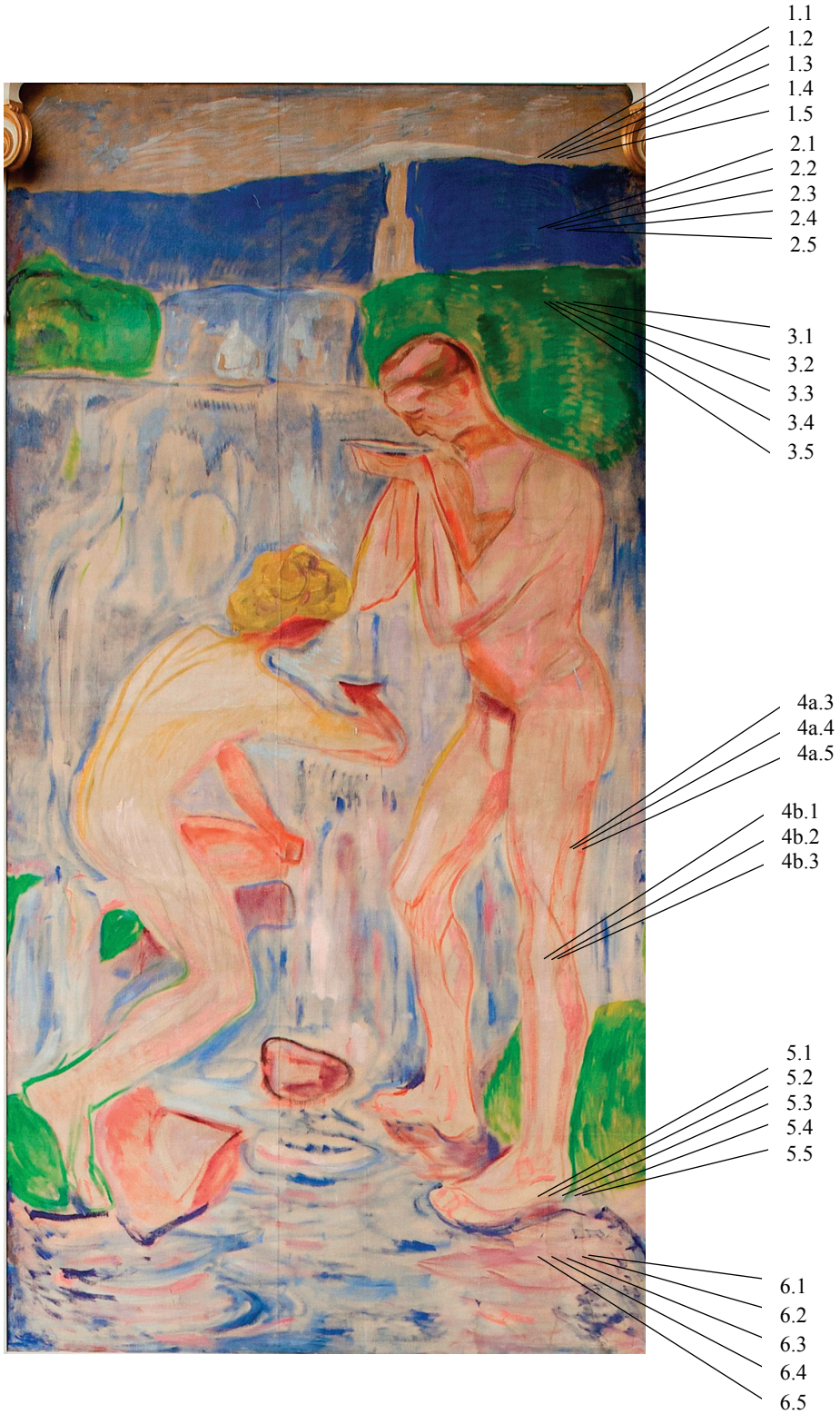



**Figure 5:** Points per transects for measurements/sampling (Photo: Terje Heiestad / UiO, 2012. © The Munch Museum / The Munch-Ellingsen Group / BONO, Oslo 2014)

areas of the sample. In this way it was possible to get a good picture of the element content of the sample.

In the following, the XRF measurements of all points for all transects are presented and shown in tables and graphs[8], and microscope photography, in both normal and UV light, of samples mounted for cross sections are presented in tables. Results of analyses from the selection of samples analysed in the SEM microscope are like the XRF measurements presented in tables and graphs for best possible reading and interpretation of the results. Further reports from the SEM-EDX analyses are presented in appendix 1, and further on the operating data on XRF measurements, including spectras, are given in appendix no 2 and 3.

[8] Not all identified elements are presented in the tables and diagrams.

*XRF measurements of all transects and points per transect*

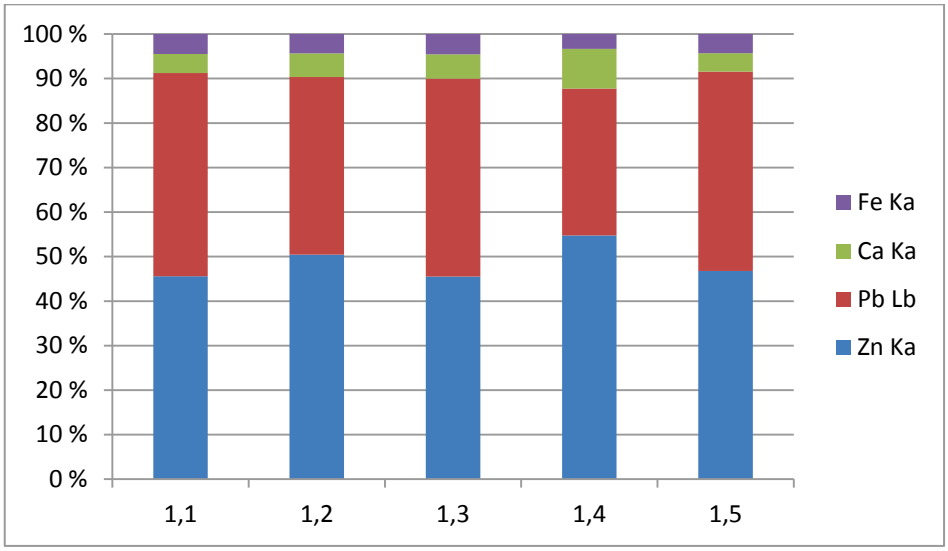
**Table 2:**

**XRF measurements from transect no 1, light blue (sky)**[9]

| Measurement from point per transect | Zn (Ka) | Pb (Lb) | Ca (Ka) | Fe (Ka) |
|---|---|---|---|---|
| **1.1** | 112,31 | 112,53 | 10,53 | 11,07 |
| **1.2** | 139,26 | 110,26 | 14,61 | 12,04 |
| **1.3** | 131,28 | 128,16 | 15,81 | 13,14 |
| **1.4** | 208,73 | 125,68 | 33,95 | 12,78 |
| **1.5** | 113,27 | 108,34 | 10,07 | 10,4 |

**Graph 2:**

**Graph presentation of XRF measurements from transect no 1, light blue (sky)**




[9] The measurements did not record any blue pigment elements, probably due to the exact area where measurements and samples were taken. In other blue areas of the painting, cobalt (Co) was registered as a main blue pigment element. The detection of Fe in the XRF measurements is thought to be connected to the instrument, and this element is also not detected in the SEM-EDX analyses of sample from the area (see further down, in presentation of SEM-EDX results)

**Table 3:**

**XRF measurements from transect no 2, blue (mountain)**

| Measurement from point per transect | Zn (Ka) | Pb (Lb) | Ca (Ka) | Fe (Ka) | Co (Ka) | Ba (Ka) | Cu (Ka) |
|---|---|---|---|---|---|---|---|
| **2.1** | 338,27 | 63,33 | 22,92 | 12,22 | 139,99 | 24,64 | 19,14 |
| **2.2** | 314 | 51,79 | 14,07 | 11,44 | 163,92 | 26,74 | 19,64 |
| **2.3** | 318,15 | 52,65 | 12,82 | 11,01 | 187,26 | 29,43 | 22,41 |
| **2.4** | 404,6 | 62,1 | 11,27 | 14,09 | 282,86 | 42,02 | 18,29 |
| **2.5** | 308,33 | 50,21 | 13,58 | 11,07 | 143,9 | 26,08 | 16,44 |

**Graph 3:**

**Graph presentation of XRF measurements from transect no 2, blue (mountain)**

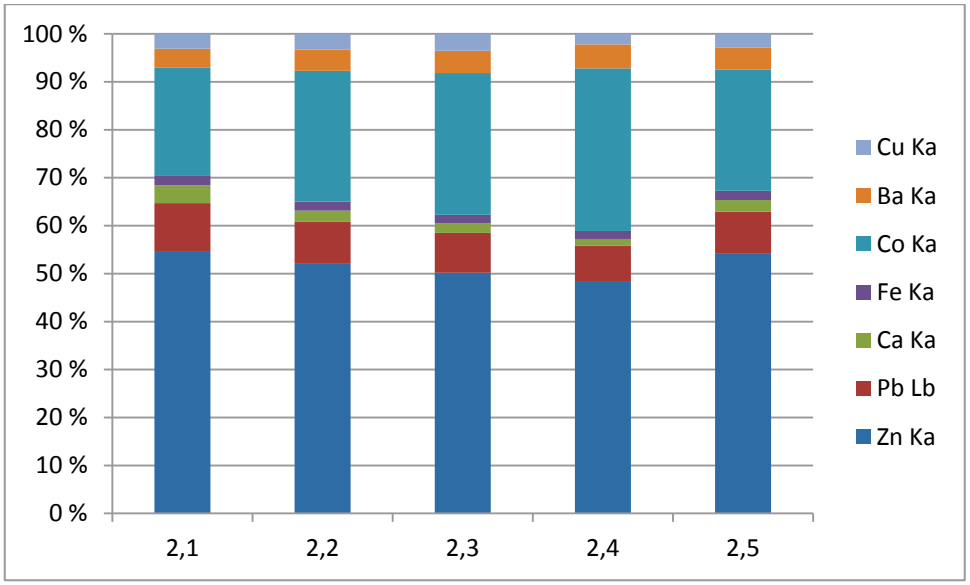


**Table 4:**

**XRF measurements from transect no 3, green (landscape)**

| Measurement from point per transect | Zn (Ka) | Pb (Lb) | Ca (Ka) | Fe (Ka) | Cu (Ka) | Cr (Ka) | As (Kb) |
|---|---|---|---|---|---|---|---|
| **3.1** | 336,19 | 79,2 | 59,87 | 18,01 | 196,14 | 82,13 | 22,01 |
| **3.2** | 44,88 | 13,91 | 3,49 | 3,39 | 50,07 | 13,46 | 6,33 |
| **3.3** | 125,45 | 29,81 | 15,5 | 8,17 | 108,35 | 41,94 | 11,91 |
| **3.4** | 105,77 | 23,07 | 9,35 | 6,49 | 93,16 | 49,62 | 10,78 |
| **3.5** | 43,98 | 13,91 | 3,56 | 3,39 | 50,07 | 13,46 | 6,33 |

**Graph 4:**

**Graph presentation of XRF measurements from transect no 3, green (landscape)**

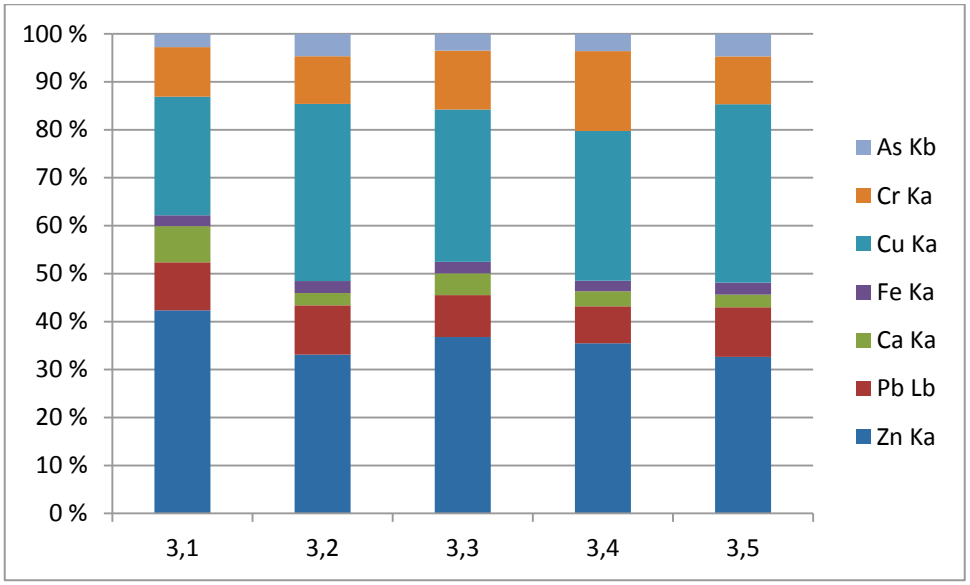


**Table 5:**

**XRF measurements from transect no 4 (4b & 4a), light red (flesh)**

| Measurement from point per transect | Zn (Ka) | Pb (Lb) | Ca (Ka) | Fe (Ka) | Cu (Ka) | As (Kb) |
|---|---|---|---|---|---|---|
| **4b.1** | 250,94 | 78,42 | 89,75 | 13,25 | 19,71 | 2,18 |
| **4b.2** | 258,24 | 85,31 | 91,76 | 13,06 | 21,49 | 2,43 |
| **4b.3** | 225,26 | 83,95 | 80,58 | 13,56 | 20,86 | 5,3 |
| **4a.3** | 183,41 | 71,5 | 68,46 | 11,06 | 17,14 | 6,64 |
| **4a.4** | 207,82 | 65,11 | 49,17 | 9,96 | 15,42 | 11,14 |
| **4a.5** | 216,67 | 62,9 | 47,88 | 10,93 | 16,49 | 21,94 |

**Graph 5:**

**Graph presentation of XRF measurements from transect no 4 (4b & 4a), light red (flesh)**

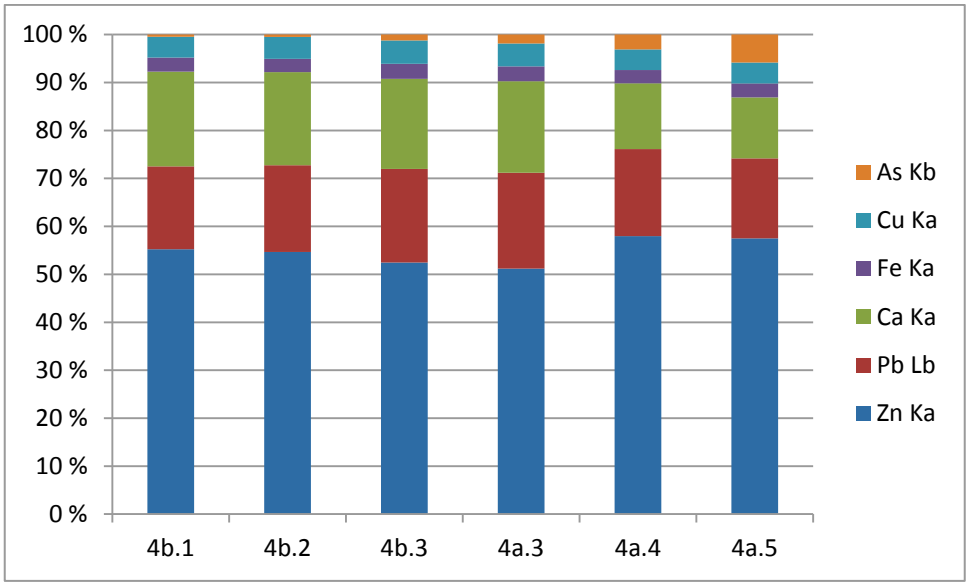


**Table 6:**

**XRF measurements from transect no 5, white/ground (heel)**

| Measurement from point per transect | Zn (Ka) | Pb (Lb) | Ca (Ka) | Fe (Ka) | Co (Ka) | Cu (Ka) |
|---|---|---|---|---|---|---|
| **5.1** | 362,83 | 98,95 | 122,33 | 16,05 | 9,25* | 24,8 |
| **5.2** | 343,87 | 103,7 | 135,15 | 18,15 | 10,11* | 26,95 |
| **5.3** | 284,41 | 105,11 | 129,4 | 15,36 | 7,81* | 23,09 |
| **5.4** | 356,6 | 106,99 | 116,39 | 15,38 | 10,5* | 24,63 |
| **5.5** | 348,73 | 113,69 | 115,98 | 15,47 | 13,84 | 24,25 |

* essentially background readings, not confirmed as "peaks"

**Graph 6:**

**Graph presentation of XRF measurements from transect no 5, white/ground (heel)**

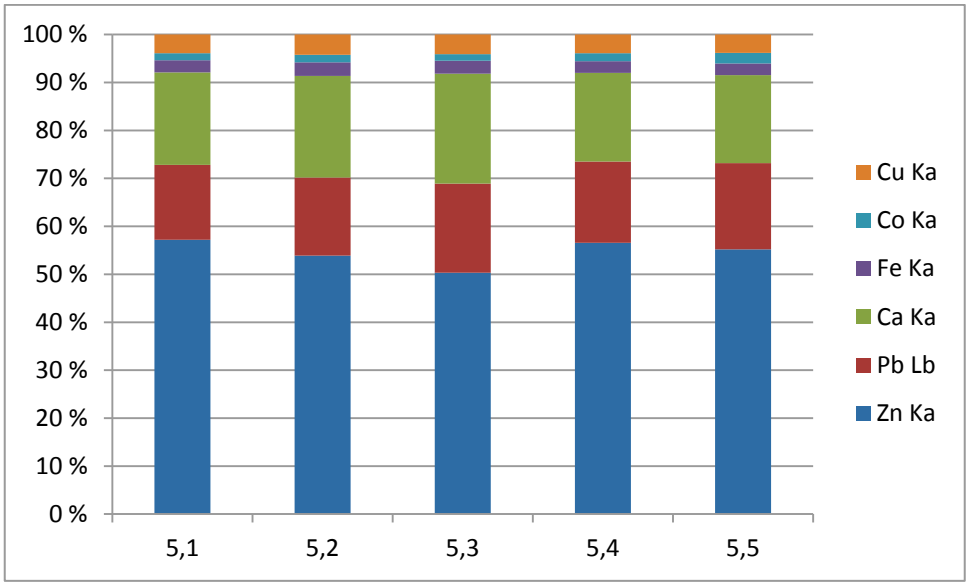


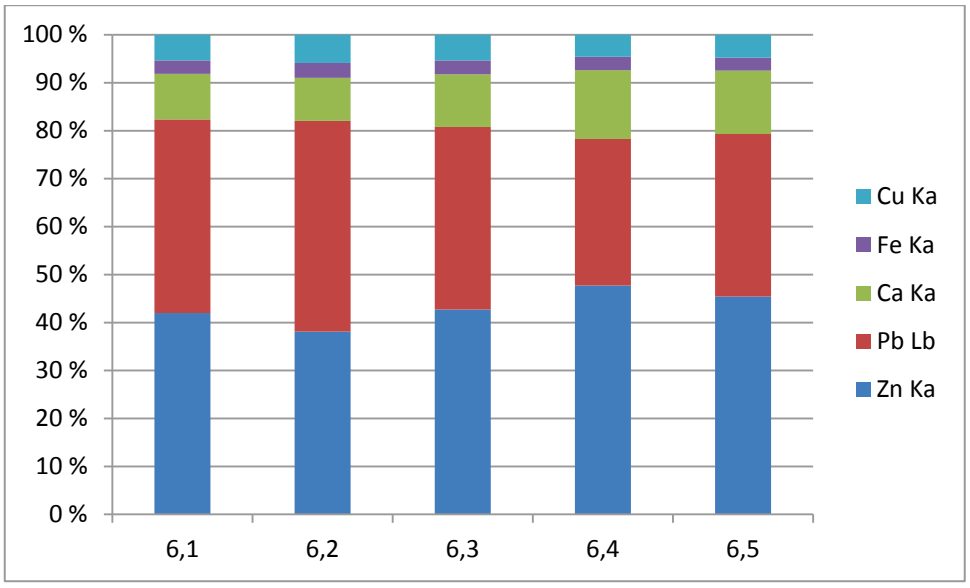
**Table 7:**

**XRF measurements from transect no 6, light purple (water)**

| Measurement from point per transect | Zn (Ka) | Pb (Lb) | Ca (Ka) | Fe (Ka) | Cu (Ka) |
|---|---|---|---|---|---|
| **6.1** | 183,82 | 176,59 | 41,67 | 12,18 | 23,41 |
| **6.2** | 153,93 | 177,51 | 36,2 | 12,54 | 23,69 |
| **6.3** | 194,31 | 173,08 | 50 | 13,23 | 24,22 |
| **6.4** | 245,73 | 157,21 | 73,9 | 14,5 | 23,48 |
| **6.5** | 226,52 | 169,04 | 65,78 | 13,56 | 23,73 |

**Graph 7:**

**Graph presentation of XRF measurements from transect no 6, light purple (water)**



*Microscopy: normal and UV light photography of mounted samples*

**Table 8: samples from transect no 1**

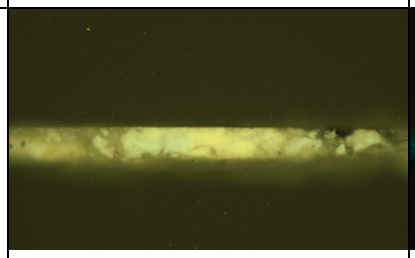
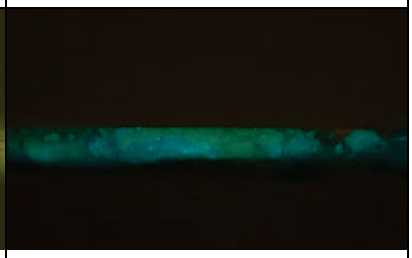
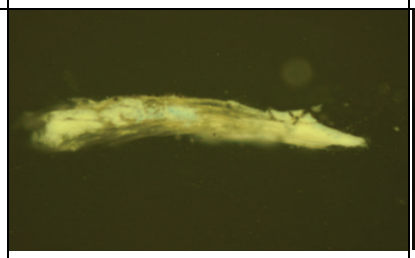
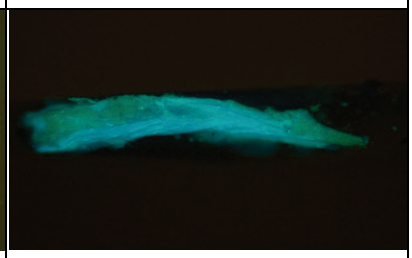
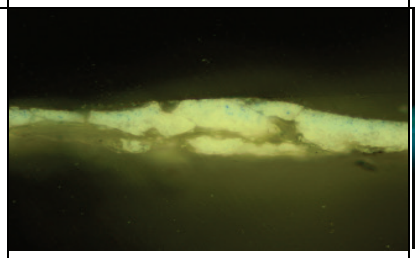
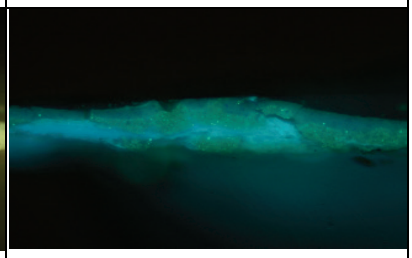
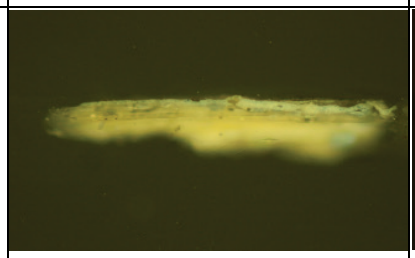
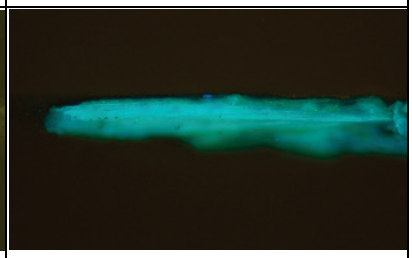
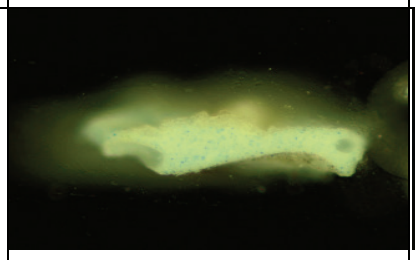
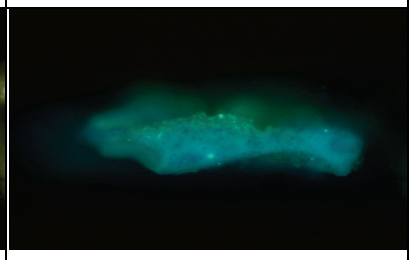
| SAMPLE NUMBER Transect:point | PHOTO, NORMAL LIGHT | PHOTO, UV LIGHT |
|---|---|---|
| **1:1** Light blue (sky) : outside tide-line, left side |  |  |
| | 10x | 10x |
| **1:2** Light blue (sky) : tide-line border zone, left side |  |  |
| | 10x | 10x |
| **1:3** Light blue (sky) : tide-line centre |  |  |
| | 20x | 20x |
| **1:4** Light blue (sky) : tide-line border zone, right side |  |  |
| | 10x | 10x |
| **1:5** Light blue (sky) : outside tide-line, right side |  |  |
| | 20x | 20x |

**Table 9: samples from transect no 2**

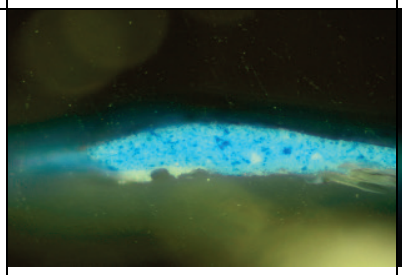
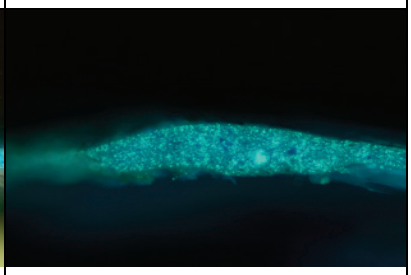
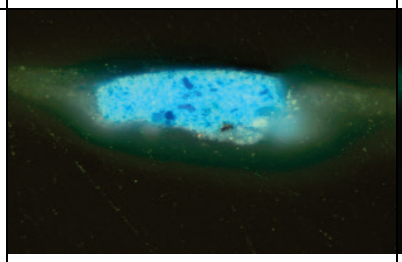
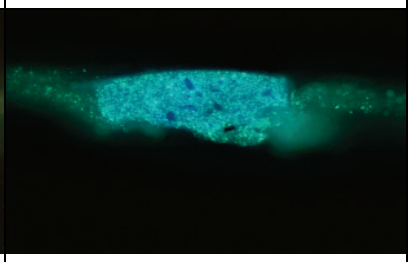
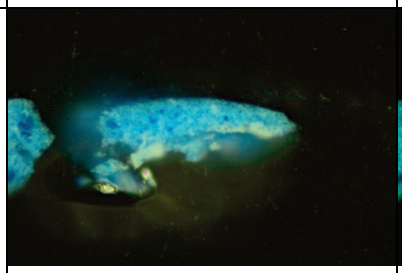
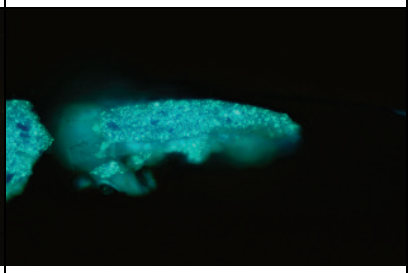
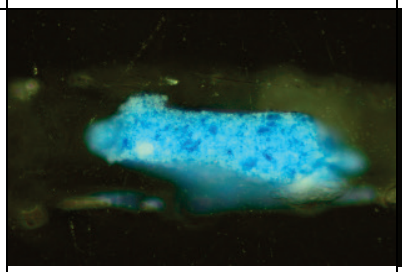
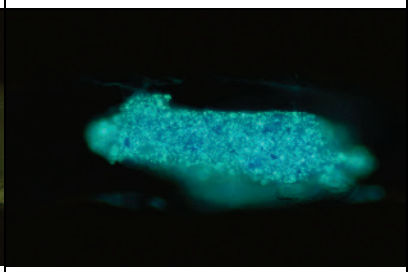
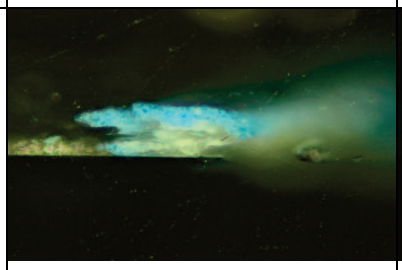
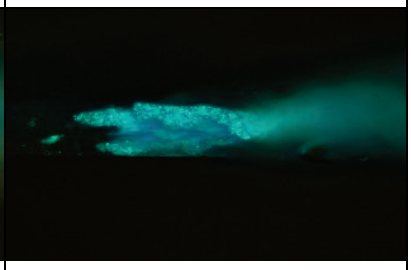
| SAMPLE NUMBER Transect:point | PHOTO, NORMAL LIGHT | PHOTO, UV LIGHT |
|---|---|---|
| **2:1** Blue (mountain) : outside tide-line, left side |  |  |
| | 20x | 20x |
| **2:2** Blue (mountain) : tide-line border zone, left side |  |  |
| | 20x | 20x |
| **2:3** Blue (mountain) : tide-line centre |  |  |
| | 20x | 20x |
| **2:4** Blue (mountain) : tide-line border zone, right side |  |  |
| | 20x | 20x |
| **2:5** Blue (mountain) : outside tide-line, right side |  |  |
| | 20x | 20x |

**Table 10: samples from transect no 3**

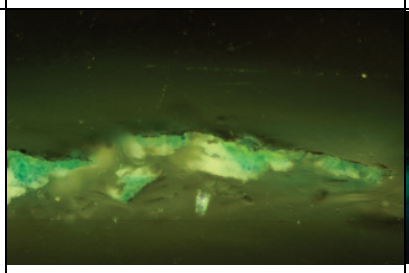
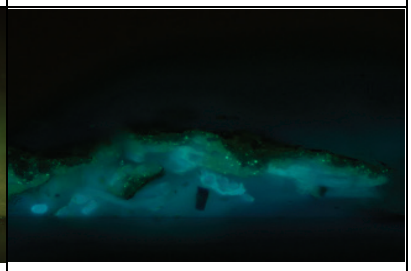
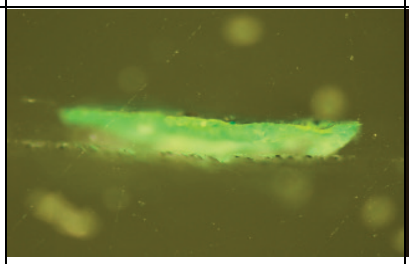
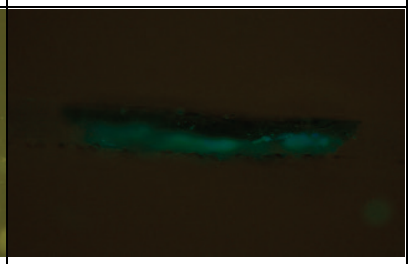
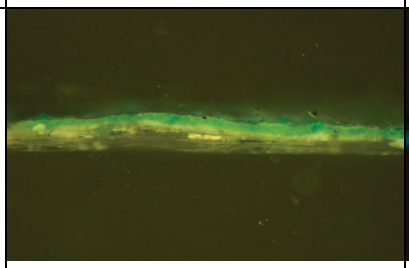
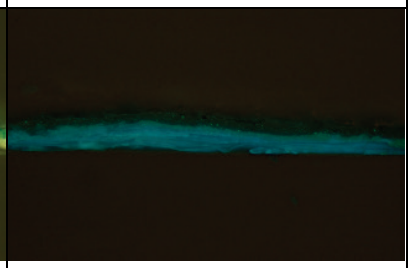
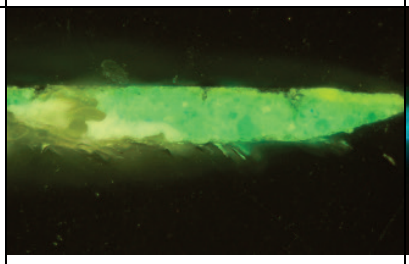
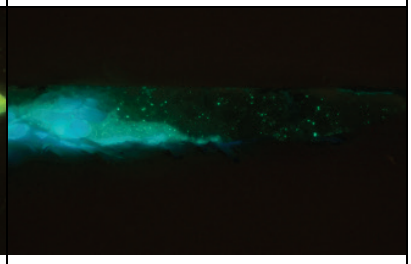
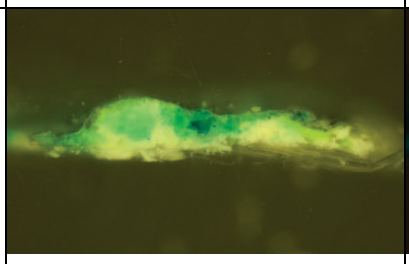
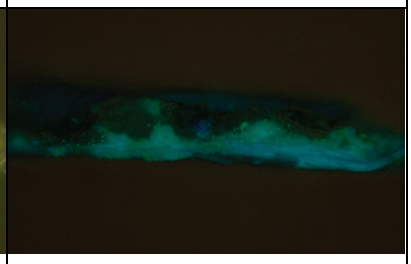
| SAMPLE NUMBER Transect:point | PHOTO, NORMAL LIGHT | PHOTO, UV LIGHT |
|---|---|---|
| **3:1** Green (landscape) : outside tide-line, left side |  |  |
| | 20x | 20x |
| **3:2** Green (landscape) : tide-line border zone, left side |  |  |
| | 10x | 10x |
| **3:3** Green (landscape) : tide-line centre |  |  |
| | 10x | 10x |
| **3:4** Green (landscape) : tide-line border zone, right side |  |  |
| | 20x | 20x |
| **3:5** Green (landscape) : outside tide-line, right side |  |  |
| | 10x | 10x |

**Table 11: samples from transect no 4 (a & b)**

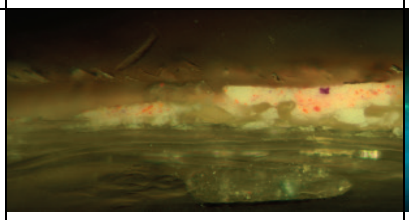
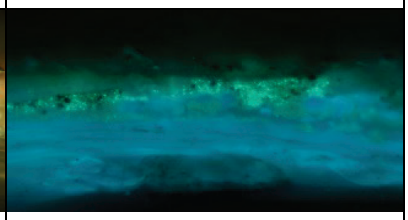
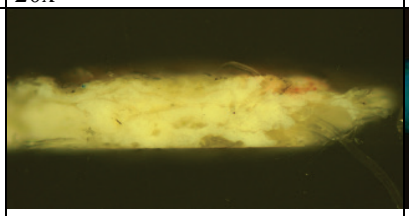
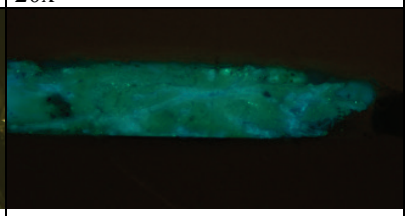
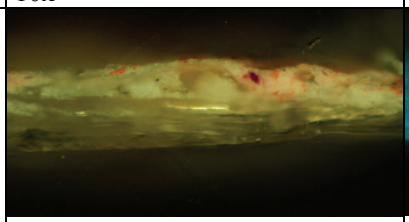
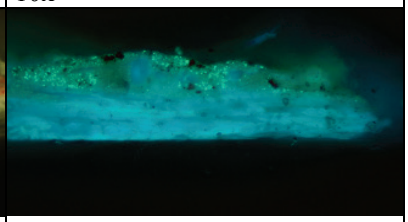
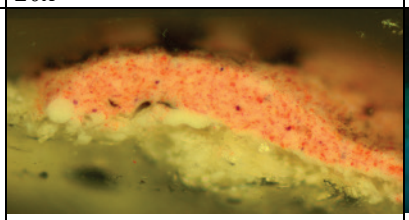
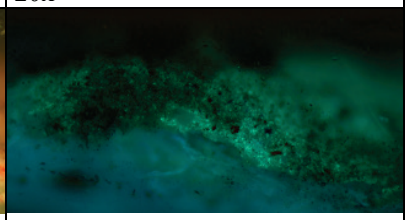
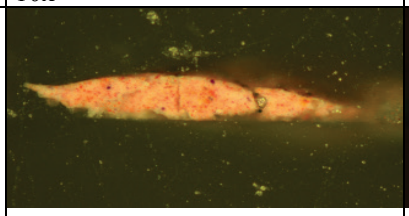
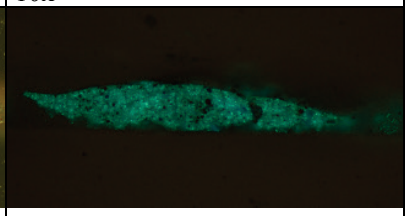
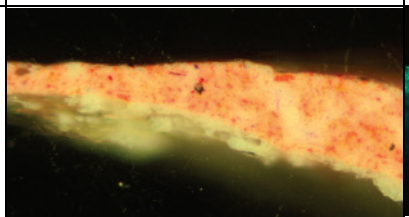
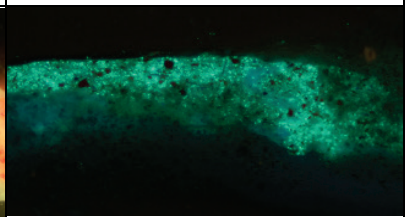
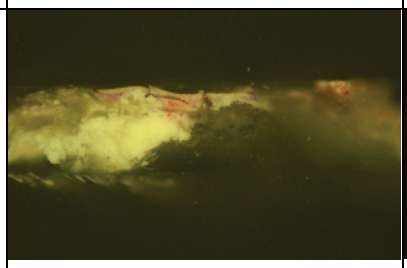
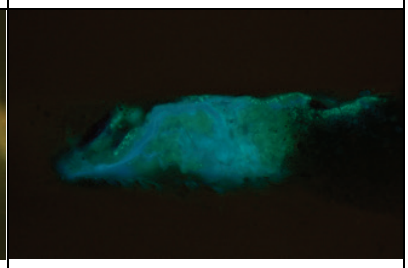
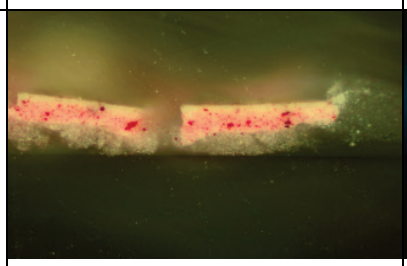
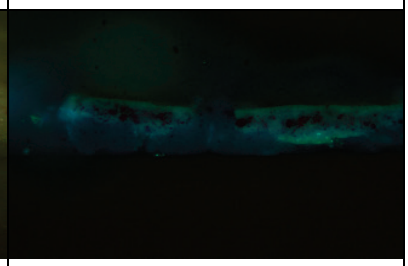
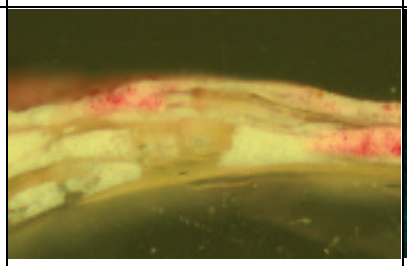
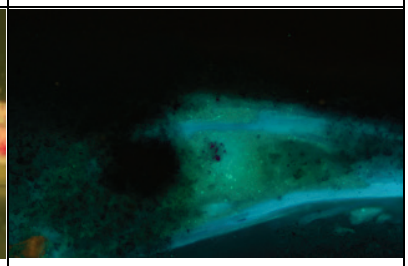
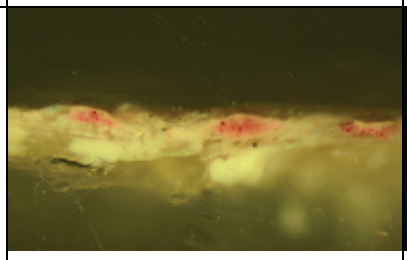
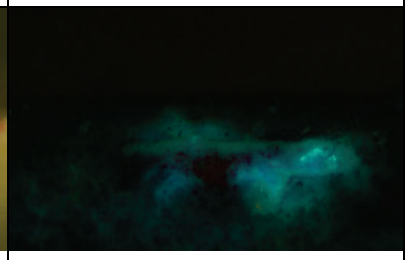
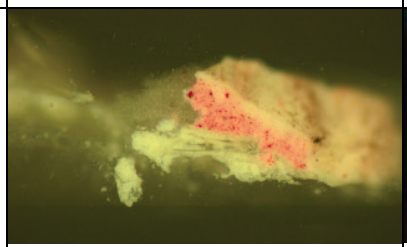
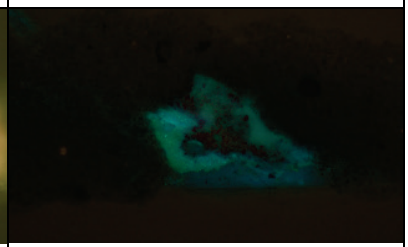
| SAMPLE NUMBER Transect:point | PHOTO, NORMAL LIGHT | PHOTO, UV LIGHT |
|---|---|---|
| **4b:1** Light red (flesh) : outside tide-line, left side |  20x |  20x |
| **4b:2** Light red (flesh) : tide-line border zone, left side |  10x |  10x |
| **4b:3** Light red (flesh) : tide-line centre |  20x |  20x |
| **4a:3** Light red (flesh) : tide-line centre |  10x |  10x |
| **4a:4** Light red (flesh) : tide-line border zone, right side |  10x |  10x |
| **4a:5** Light red (flesh) : outside tide-line, right side |  20x |  20x |

**Table 12: samples from transect no 6**

| SAMPLE NUMBER Transect:point | PHOTO, NORMAL LIGHT | PHOTO, UV LIGHT |
|---|---|---|
| **6:1** Light purple (water) : outside tide-line, left side |  |  |
| | 10x | 10x |
| **6:2** Light purple (water) : tide-line border zone, left side |  |  |
| | 20x | 20x |
| **6:3** Light purple (water) : tide-line centre |  |  |
| | 20x | 20x |
| **6:4** Light purple (water) : tide-line border zone, right side |  |  |
| | 10x | 20x |
| **6:5** Light purple (water) : outside tide-line, right side |  |  |
| | 10x | 10x |

*SEM-EDX analyses of mounted samples (1.1- 1.3; 2.1-2.3; 3.1- 3.3)*

**Table 13:**

**SEM-EDX analysis from transect no 1, light blue (sky) (measurements in atom%)**

| Sample from point per transect | Zn | Pb | Ca |
|---|---|---|---|
| **1.1** | 0,81 | 1,07 | 0,61 |
| **1.2** | 1,6 | 0,56 | 1,04 |
| **1.3** | 1,32 | 0,71 | 0,84 |

**Graph 8:**

**Graph presentation of SEM-EDX analysis from transect no 1, light blue (sky) (measurements in atom%)**

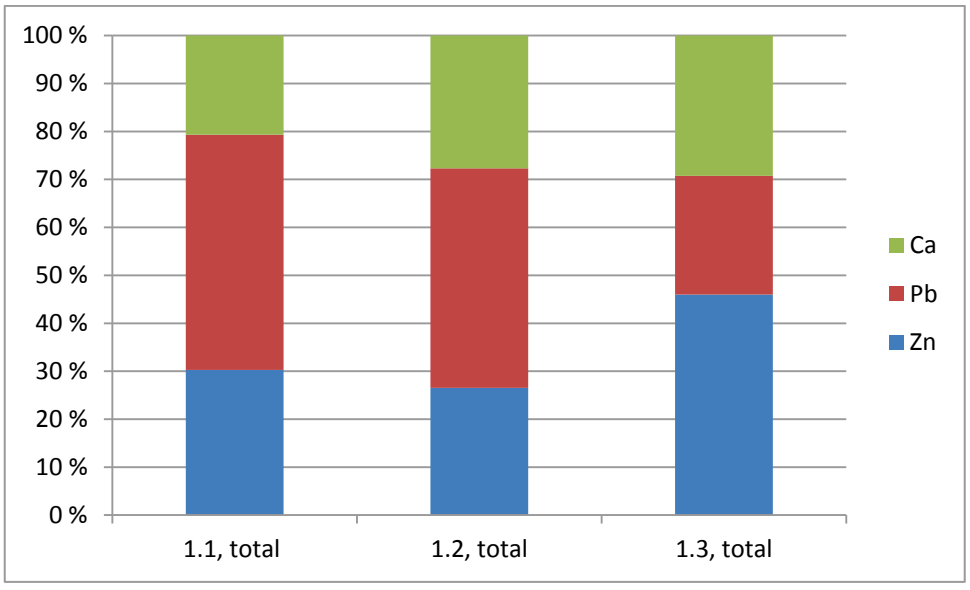


**Table 14:**

**SEM-EDX analysis from transect no 2, blue (mountain) (measurements in atom%)**

| Sample from point per transect | Zn | Pb | Ca | Fe | Co | Ba | Cu | Al | S |
|---|---|---|---|---|---|---|---|---|---|
| **2.1** | 5,37 | 0,55 | 0 | 0 | 1,06 | 0,31 | 0 | 3,04 | 0,31 |
| **2.2** | 2,86 | 0,3 | 0,07 | 0,03 | 0,77 | 0,28 | 0,07 | 2,1 | 0,35 |
| **2.3** | 3,35 | 0,45 | 0,13 | 0 | 1,5 | 0,43 | 0,21 | 2,18 | 0,51 |

**Graph 9:**

**Graph presentation of SEM-EDX analysis from transect no 2, blue (mountain) (measurements in atom%)**

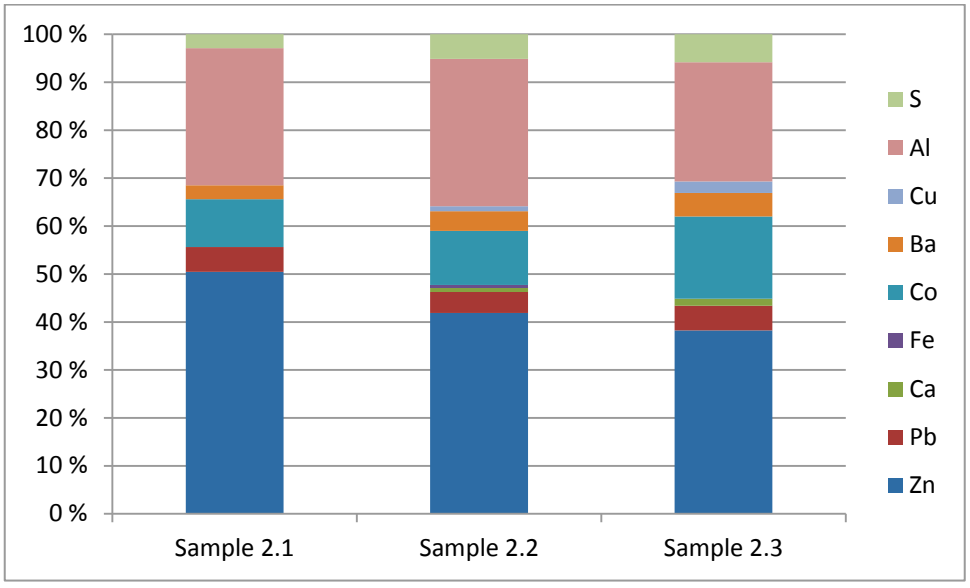


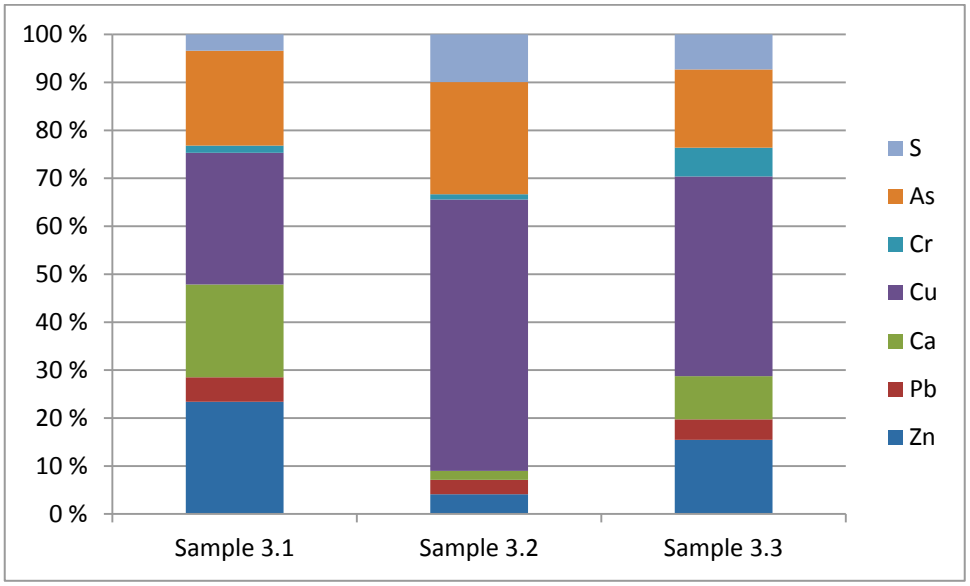
**Table 15:**

**SEM-EDX analysis from transect no 3, green (landscape) (measurements in atom%)**

| Sample no | Zn | Pb | Ca | Cu | Cr | As | S |
|---|---|---|---|---|---|---|---|
| **3.1** | 1,1 | 0,24 | 0,91 | 1,29 | 0,07 | 0,93 | 0,16 |
| **3.2** | 0,26 | 0,19 | 0,12 | 3,58 | 0,07 | 1,48 | 0,63 |
| **3.3** | 0,36 | 0,1 | 0,21 | 0,97 | 0,14 | 0,38 | 0,17 |

**Graph 10:**

**Graph presentation of SEM-EDX analysis from transect no 3, green (landscape) (measurements in atom%)**



When comparing examples of the XRF measurements and SEM-EDX analyses of the same transect and points per transect of the tide-line areas, it can be understood in the way that some change and movement of the elements in the paint layer has taken place. Even if it can be difficult to read out a clear pattern on how the different materials and elements of the paint layer behave when affected by water, it is quite clear that some movements and some alterations have taken place regarding some of the materials. Further interpretations of the readings are presented in the following chapter, on *Discussion.*

*PH measurements*

A first round of pH measurements have been performed, using a pH meter with a flat Sentron probe for surface measurements (borrowed from The National Archives, K. Ramsholt). These measurements gave no significant results, and follow- up pH measurements should therefore be performed using for instance a *HORIBA Twin Compact* pH meter and interpreting the results using a *ISO 3071:2005* standard (Personal correspondence, T. Frøysaker, Conservation Studies, University of Oslo. 12th Feb / 10th May 2012). The pH measurements of the affected areas of *The Source,* compared to measurements of unaffected areas of the painting, might enhance the appearance of what material changes could have occurred in the areas. Earlier registrations of tide-lines on paper materials shows that the formation of tide-lines often is followed by a change of pH in the affected area (Hutchins, 1983:58). A change in pH may also be of significance to the affected pigments and painting materials in general, and a registration of this will therefore be important in order to see whether the materials might have undergone any change at the different stages of the tide-line.

Description of measurement areas and results of the undertaken pH measurements are given in appendix no 4.

## DISCUSSION

The first hand examination of the tide-line area using UV illumination as well as a Dino Lite hand-held microscope, gave clear indications that the tide-line area displayed certain differences compared to the unaffected areas of the painting. The tide-line is distinguished by lighter fluorescence, especially along the rim of the tide-line area. Likewise, images of the tide-line area using a Dino Lite microscope seem to show that some materials have been shuffled in the area, showing accumulation of some material along the rim of the tide-line and depletion of material in other areas.

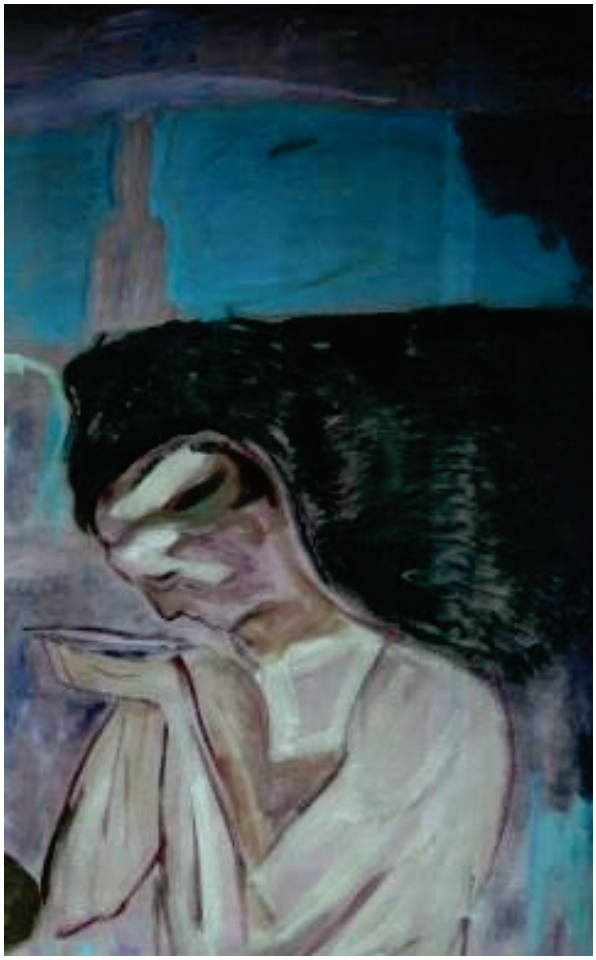


**Figure 6:** Detail UV photo of area with tide-line on upper parts of *The Source* (Photo: K. Scharffenberg, 2010).

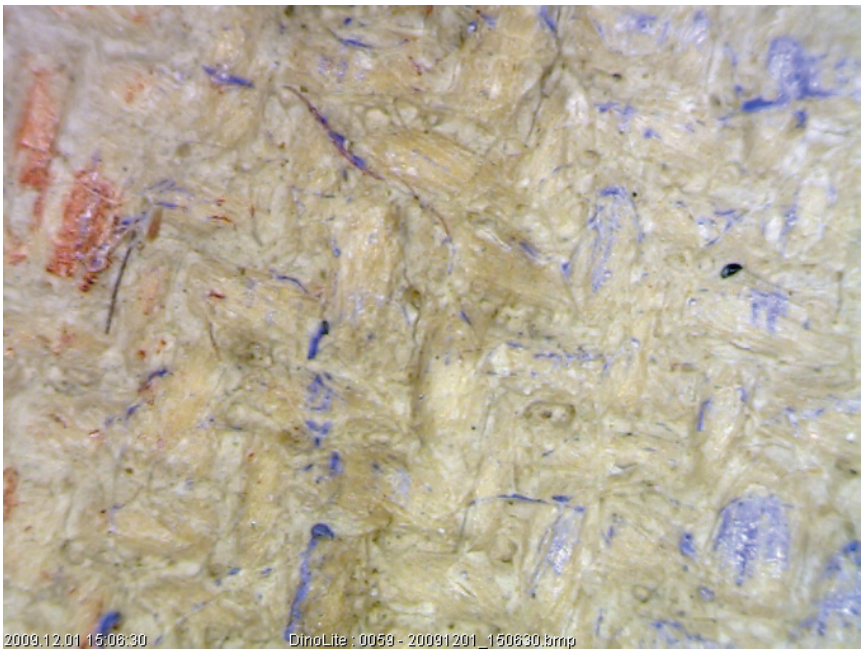



**Figure 7:** Detail Dino Lite photo of dark edge of tide-line on *The Source* (Photo: K. Scharffenberg, 2010).

As seen in the above presented XRF measurements and SEM-EDX analyses from the tide-line area, they seem to indicate that the content of some of the main elements in the area vary to a certain extent at the different stages of the tide-line, which is outside, inside and in the border-zone of the tide-line. Unn Plahter observed something similar when investigating the tide-line on *The Scream*. Plahter's unpublished studies from 2008 show, for instance, a difference in the concentration of Zn, Pb, Ca, S and Cl when comparing the areas along the tide-line edge and the areas outside and inside the tide-line edge (Plahter, 2008).

The detected differences in the element amount at different points per transect of the tide-line on *The Source* can of course be coincidental, according to, for instance, the measurements and sample locations. It is still thought that it is possible to read out a certain pattern of differences in the undertaken measurements, which could be a topic for future research.

In the above presented readings of elements in transect no 1, the differences noted in the concentration of both Zn, Pb and Ca at the different points indicate that these must have been soluble in the water and migrated with the fluid front. In addition, the measurement of the larger amount of Zn in the tide-line border (here point 1.2) could indicate a development of the earlier registered surface materials on the paintings, like the Zn oxalates, in the areas affected by high relative humidity. On the other hand, the measurements and analyses made at the different points of transects no 2 and 3 seem to show a lowered Zn content both in the middle and in the rim of the tide-line. This could indicate both a physical and chemical intervention on the elements, as both particles and alteration products, as for instance oxalate salts, could be washed away by the running water. The readings from transect 2 and 3 also show similar differences according to contents of other elements, such as Pb, Ca and Co. In some instances the element content seems to increase in the areas where water has influenced the painting materials, while it in other instances seems to decrease. In transect no 2, both Zn, Pb, Co and Al contents seem to be lowered in the rim of the tide-line. Also in the middle part of the tide-line area, the Zn content seem to be lowered, while the content of Pb, Co and Al seems to be heightened in this area. Also the S content shows here heightened values in the mid area of the tide-line. In transect no 3, Zn, Pb and Ca contents seem to be lowered both in the middle and in the rim of the tide-line area, while Cu and As contents seem to be lowered in the middle part of the tide-line area and heightened in the rim of the area. The S content also shows here heightened values in the rim of the tide-line area. The XRF readings of transects no 4, 5 and 6 show similar signs of some alterations of the element content in the tide-line area, even if these readings are more ambiguous and less clearly readable. In transect no 5, the Zn content seems for instance to be quite a bit lowered in the middle of the tide-line area, while the Cu content seems to be lowered in the middle and somewhat heightened in the rim of the area. In transect no 6, on the other hand, the Cu content seem to be somewhat heightened in the middle of the tide-line area.

Although the readings do not show a totally clear pattern regarding reactions and movements of elements in the affected area of the painting, the fact that some movement can be traced and that some alteration seems to have taken place in one or another way may tell us

that the water running over the painting has affected some of the material. Especially concerning paint layers with pigments like zinc white and ultramarine (containing Al, amongst other substances) it will be relevant to bear in mind the hygroscopic properties of these pigments when looking at the reaction pattern of the elements in the paint layer. The same applies for the Ca containing ground. As seen in the readings done on the transects of the tide-line area in *The Source*, alterations can be traced both concerning Zn, Al and Ca content in the different sections of an affected area. This might be related to the hygroscopic qualities of pigments containing these elements (like zinc white and ultramarine) as well as to the fact that little binding medium binds and protects the particles from water. The reaction of painting materials to water might thus be both a chemical reaction, according to the hygroscopic properties of the present elements, and a more physical reaction where leanly bound particles are transported by the water.

Alterations can also be seen regarding elements contained in less hygroscopic pigments, like the Pb in lead white. Plausible explanations regarding the different properties and behaviour of the different pigments, containing different elements, should be subject to closer investigations in any further research on the tide-line topic.

Despite the ambiguities and difficulties related to the interpretations of measurements and analyses done on the tide-line area on *The Source*, all undertaken registrations may serve as a basis for future research and reinterpretations. The main goal for the analyses has been to gain a better understanding of the elements present in the different stages of the tide-line zones, and to detect any possible change or displacement of the elements between the different zones. It is obvious that the investigated area in fact represents a very complex chemical problem that requires an in-depth knowledge in order to be fully understood. Still, it is hoped that, by trying to look into the material situation in the area, this study might bring paintings conservators one step closer to an understanding of what processes and alterations we can assume to have taken place in the tide-line zone.

## CONCLUSIONS

The investigations and analyses of the tide-line on *The Source* have shown that an unvarnished, mainly medium poor paint surface like the one on Munch's painting will be especially vulnerable towards water damages. The surface will have strong chromatographic, capillary properties, enhancing the attachment of dirt to the surface as water is introduced, and at the same time exposing the pigment particles of the paint, making them especially susceptible to water and moisture reactions, both chemically and physically. The content of pigments such as zinc oxide in the paint may contribute to a particularly weak and water-susceptible paint, as will also apply to paints containing ultramarine and other hygroscopic pigments. The results from the analyses of the tide-line on *The Source* indicated that the content of some particles in the paint layers, like the Zn particles, varied to some extent between unaffected and affected areas of the tide-line. Thus, the results indicate that water running over the paint layers will affect the paint materials and cause changes in the composition of the paint, such as decreased or elevated levels of elements. This demonstrates the possible effects of water on the paint materials in terms of displacement and alteration of components.

A better knowledge of the materials present in Munch's work, and the condition and plausible sensitivity of some of the exposed surfaces of the works, may help conservators when treating his works in different ways. The results from the investigations and analyses of the tide-line on *The Source,* and possible further research concerning the tide-line questions, are thus of significance to studies concerning Munch's painting techniques and handling methods.

The outcomes of the investigations of the tide-line on *The Source* are also of significance to decision-making concerning conservation treatment of areas with similar kinds

of damages. In gaining a broader understanding of what might have happened to the materials in the affected area, the best basis for deciding whether or not to treat the damage is provided, and a more qualified decision can be made concerning what methods and materials should be used if a treatment of the area is to be carried out.

Treatment of tide-lines, whether on paper, textile or paintings, have so far often implied the use of water to eliminate or move the brown lines the damages have produced. A broader look at the results of water damage to the materials of paintings suggests that this is inaccurate. This study is a foundation for evaluating and deciding if tide-lines represent an ongoing degradation process and whether treatments with water or other kinds of treatments on these areas will be efficient, secure and ethical.

### *Wanted patination or unwanted alterations*

Although it is known that Munch gave some of his paintings a wanted patination through outdoors weathering, it is hard to believe that the artist wanted his paintings to become obscured by dirt and inherent changes in the materials due to damages and poor display conditions. Munch's reported preferences for lightly tuned, fresco-like expressions, achieved amongst others by a heavy exposure of his paintings to outdoor settings, might not imply that the painter also included dirt and other discolouring, distorting elements to his wanted effects. Still, the uncertainty of whether Munch incorporated dirt into his work, accepting it as a part of the complete image, or not might in some instances have to be taken into account. The lack of a clear interface between the original work and unwanted dirt is according to Perry (1990) a determining factor for the extent in which a work can be safely cleaned (Perry, 1990:4). By analysing and determining the material aspects of the tide-lines on *The Source*, it still may be possible to suggest whether unwanted alterations of the paint materials are present.

In trying to put in place at least a few of the puzzle pieces in the total picture of water damaged areas, this can form the basis for understanding the mechanisms undergone in a tide-line. Even if the question still remains whether the condition of Munch's water stained paintings is related to an artistic intention and to what extent the damages have affected, and might still be affecting the painting materials, it is hoped that the undertaken studies and analyses might aid future interpretations and decisions concerning handling and treatment of paint damages like the tide-line on *The Source.* It should be of interest to painting conservators in general and Munch researchers in particular.

### *Further research*

The analyses undertaken by SEM-EDX, as well as the incomplete analyses conducted with FTIR and RAMAN microscopy, should be followed up for a further and deeper understanding of the mechanisms undergone in the tide-line area. While new analyses undertaken on the tide-line area should preferably be conducted using non-invasive techniques, the collection of samples already taken from the area will also open up possibilities for Raman studies in particular. With regard to the deposited material in the tide-line it will be useful to know whether it represents a damaging factor to the surface material in the painting, causing for instance mould growth.

The investigations and analyses undertaken in this study has in many ways been dictated by certain limitations concerning choice of analytical instruments, as well as limits of time, as some analyses and especially their interpretations will require broader investments and scientific collaboration. Further in-depth studies of the surface properties of the tide-line area in *The Source* would be desirable. The studies may include further investigations of elemental compositions in the area, including elaborated studies of the properties of the

different elements, as well as complementary research of the binding media in the layers of the area. Although the dry and lean character of the paint in *The Source* makes the investigations of particle position and disposition in the tide-line area most interesting in this case, it will also be of significance to look at the situation for the organic components in the area as the different constituents will influence each other mutually.

## POSTSCRIPT: THE FLORENCE FLOOD

The Florence flood of 1966 caused severe water damage to a vast amount of Europe's greatest art, but was also an incident which both stimulated and served as a "catalyst" for the development of several conservation methods. As reported by one of the conservators of the time, new restoration approaches were developed as direct results of specific situations: "It cannot be denied that great advances were made in restoration techniques in Florence and Italy after the flood. (…) The flood stimulated research into new methods of restoration; it also served as a catalyst, creating the ideal conditions in which to put into practice and accelerate certain procedures and reactions (…)" (Bonsanti, 2009:111). Extraordinary treatment challenges, regarding for instance paintings that had been covered up to two-thirds of their height in water, were solved through achievements only possible through a global approach to the specific problems, always considering the work in the context of its immediate environment (Bonsanti, 2009:114). The extreme situation resulted in an extraordinary solidarity amongst restorers worldwide, generously sharing their expertise and responding fully to the urgent need for help (Bonsanti, 2009:112).

The mark from a tide-line occurring on a piece of art can in many ways be seen as a result of a "quiet" flood, running over and through the materials as the damage in many ways may be equally devastating. Like the water damages from the Florence flood gave a catalytic after effect, the conservation problems resulting from tide-line damages can serve as a base for new investigations and a new understanding of how water affects different materials in order to develop the best strategy for treating the objects. The main question of whether or not a water damage on a painting can be treated should ideally be evaluated on the basis of an in depth understanding of the damage in question. The decision of leaving a paint damage untreated should be based on just as much forehand knowledge as when we decide to treat a painting. And if we decide to do a treatment, the choice of methods and materials for

treatment should be based on a careful selection. The use of water treatment for elimination of tide-lines on paintings can be seen as a method based mainly on traditions and aesthetic concerns. Given that water can disturb painting materials profoundly, and may cause severe damage to the materials, water should be used cautiously, if at all.

**ACKNOWLEDGEMENTS**

Special thanks of gratitude go to Professor Tine Frøysaker at the Conservation Studies, University of Oslo, who put me on track of the tide-line issue connected to the Munch Aula Paintings; to Head Engineer Duncan Slarke at the Conservation Studies, University of Oslo, and Associate Professor Hartmut Kutzke at The Museum of Cultural History, University of Oslo, for their invaluable help regarding undertaken measurements and analyses, including setup of tables and diagrams; to Paintings Conservator Anne Milnes for her great help in structuration and proofreading of text; to Dr. Patrick Dietemann at the Doerner Institut, München, and Dr. Marion F. Mecklenburg at the Smithsonian Museum Conservation Institute for sharing advices of great value; and last but not least to Associate Professor Noëlle L.W. Streeton at the Conservation Studies, University of Oslo, for her great supervision and guidance, inspiration and help in keeping up spirits and focus throughout the research and writing process.

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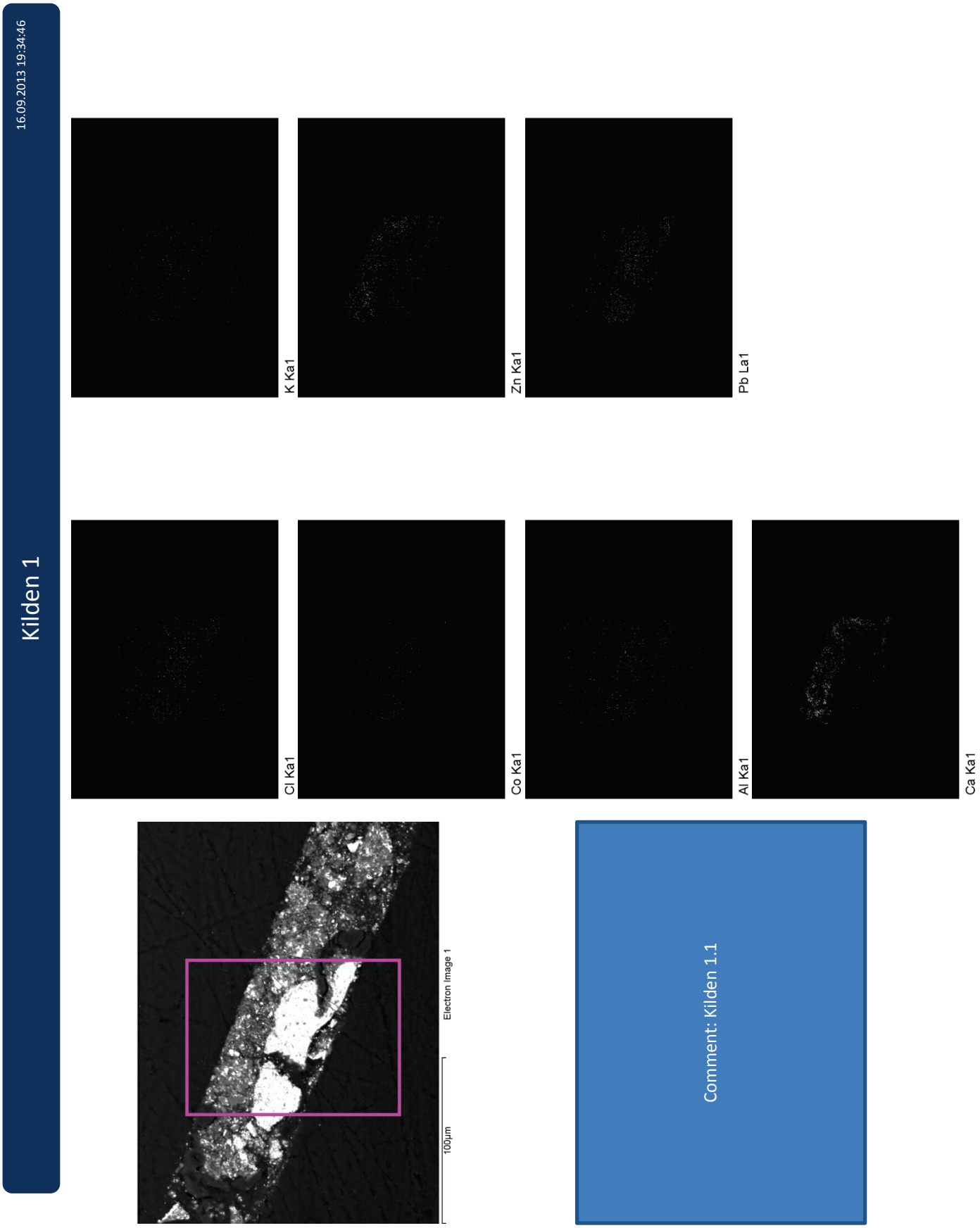
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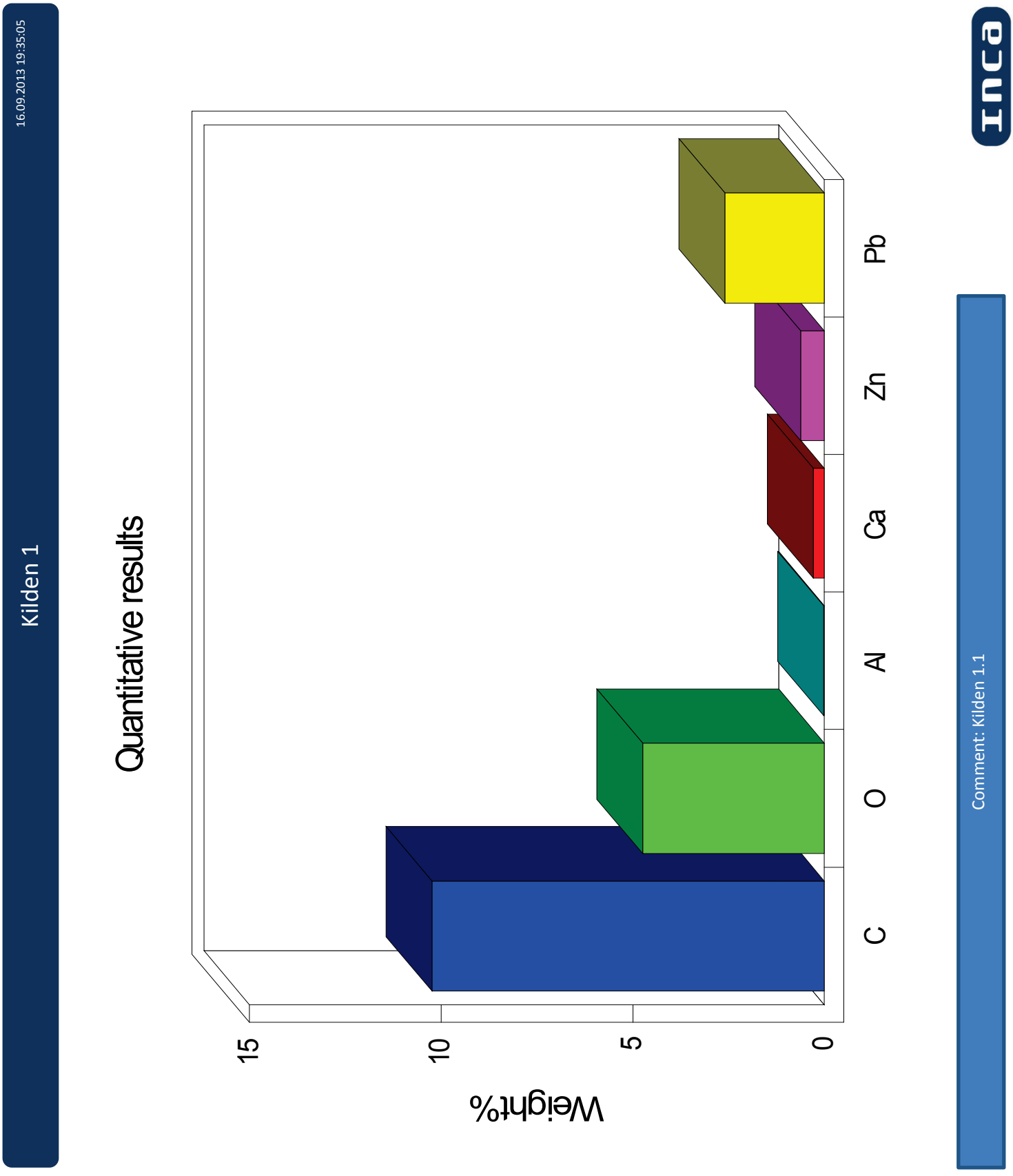
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Comment: Kilden 1.1
Inca

# Kilden 1

16.09.2013 19:35:45

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 3

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

Al Al2O3 1-jun-1999 12:00 AM

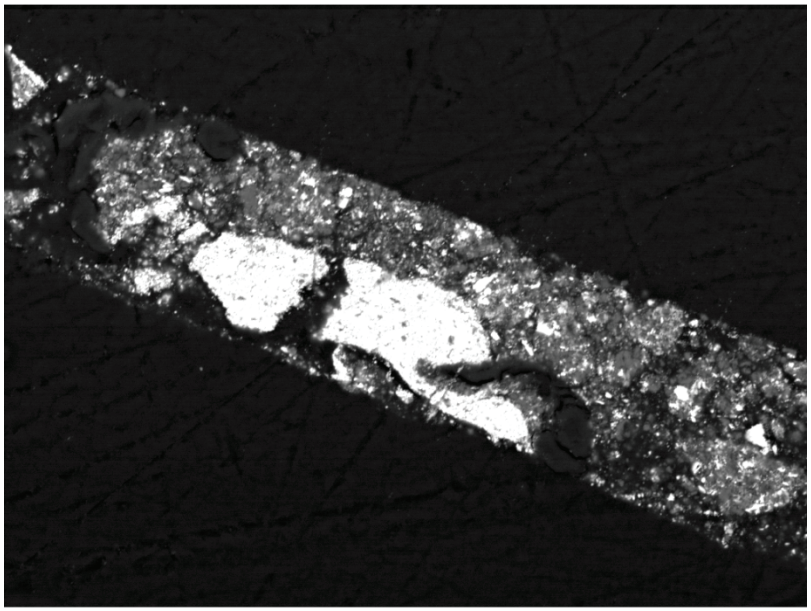
Ca Wollastonite 1-jun-1999 12:00 AM

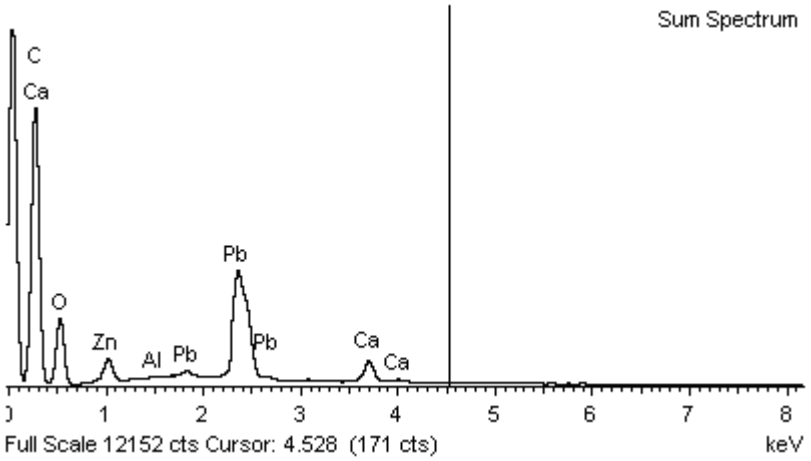
Zn Zn 1-jun-1999 12:00 AM

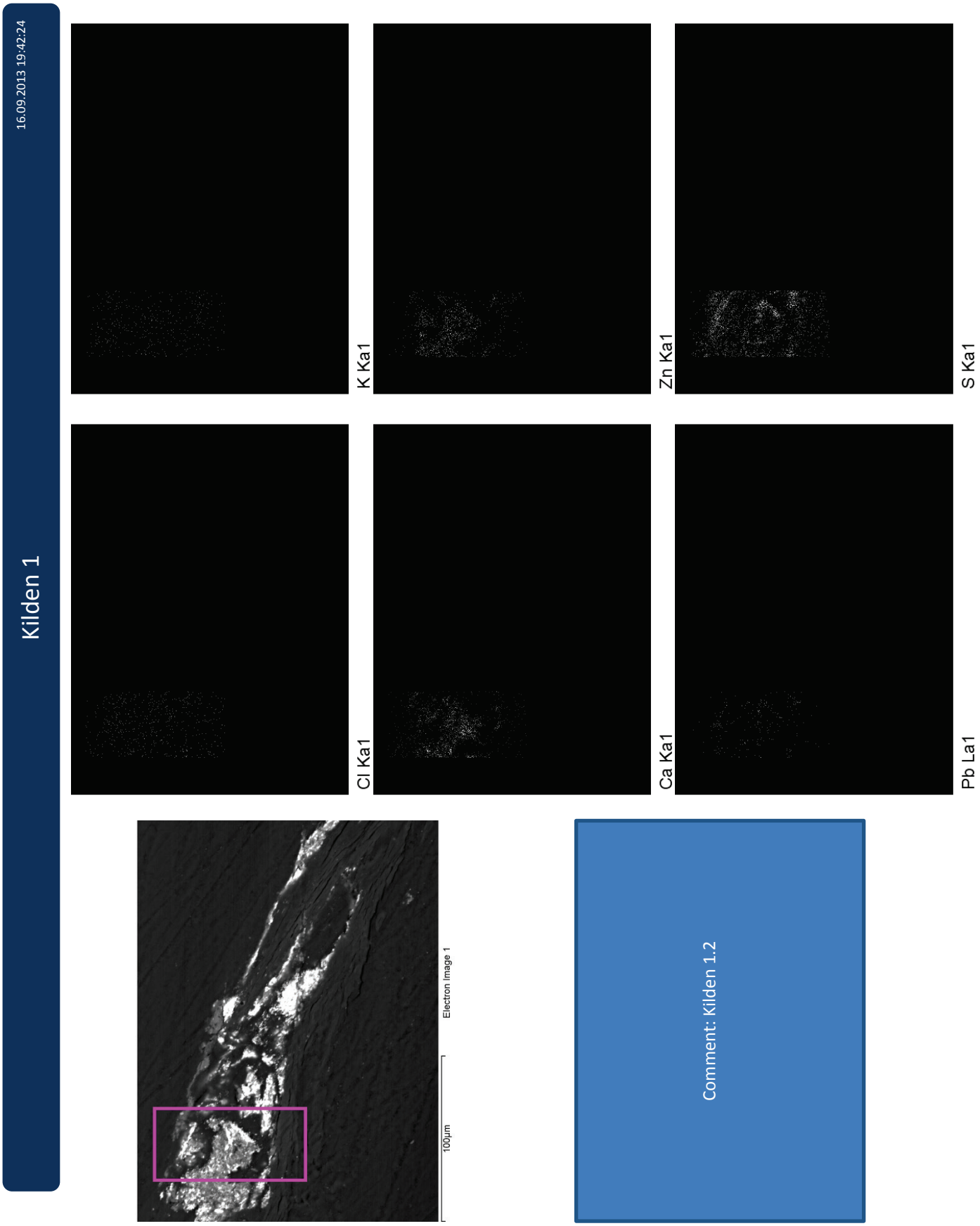
Pb PbF2 1-jun-1999 12:00 AM

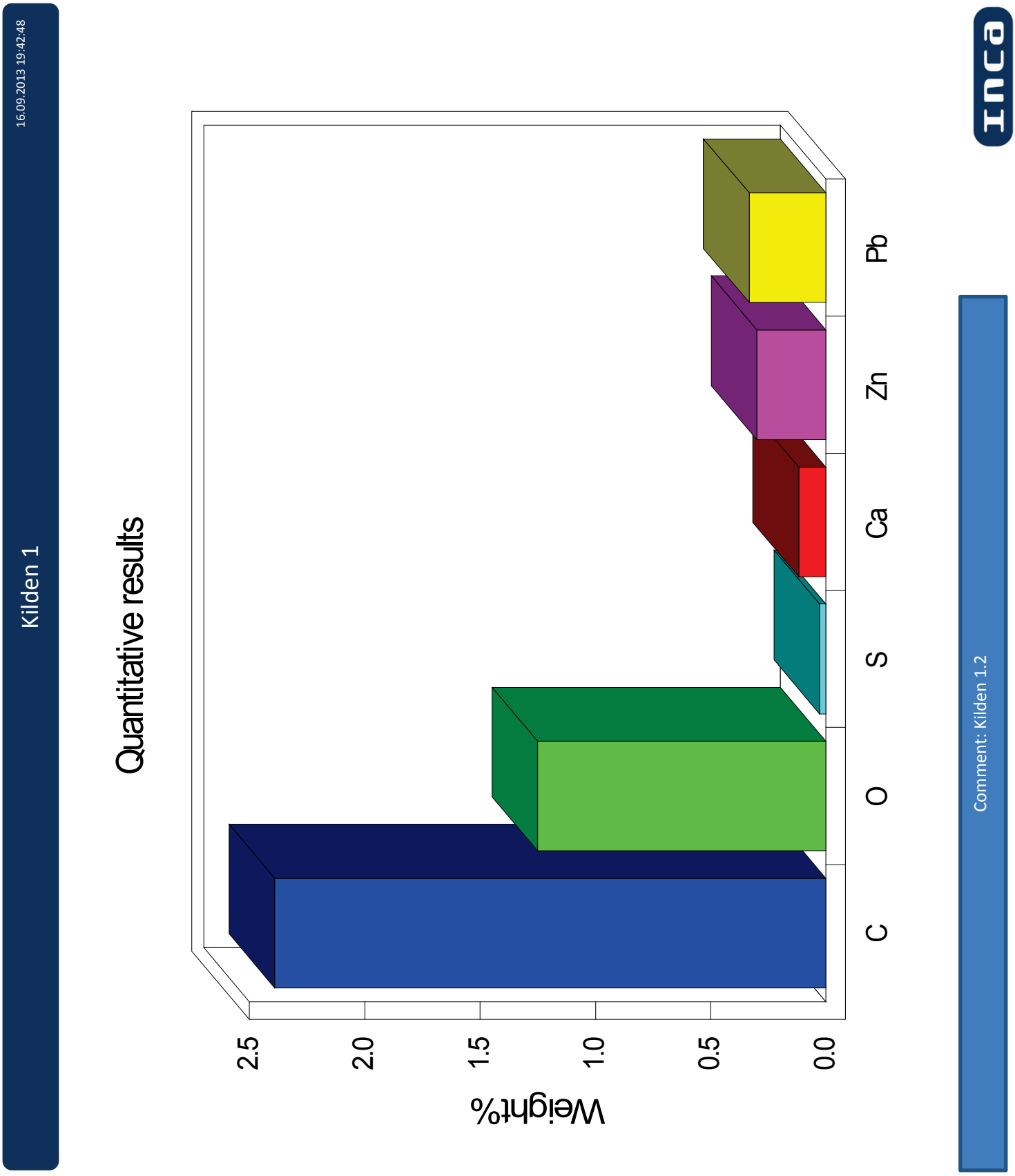
| Element | Weight% | Atomic% |
|---|---|---|
| C K | 10.24 | 72.32 |
| O K | 4.74 | 25.13 |
| Al K | 0.02 | 0.06 |
| Ca K | 0.29 | 0.61 |
| Zn K | 0.63 | 0.81 |
| Pb M | 2.60 | 1.07 |
| Totals | 18.52 | |

Comment: Kilden 1.1




Kilden 1
16.09.2013 19:42:24
Cl Ka1
K Ka1
Ca Ka1
Zn Ka1
Pb La1
S Ka1
Electron Image 1
100µm
Comment: Kilden 1.2
inca


16.09.2013 19:42:48
Kilden 1
Quantitative results
Weight%
2.5
2.0
1.5
1.0
0.5
0.0
C
O
S
Ca
Zn
Pb
Comment: Kilden 1.2
Inca

# Kilden 1

16.09.2013 19:42:55

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 3

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

S FeS2 1-jun-1999 12:00 AM

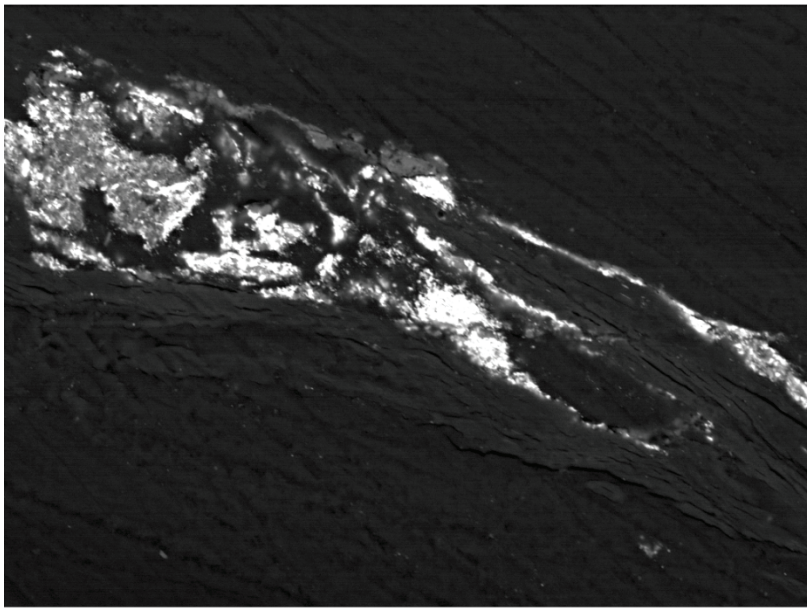
Ca Wollastonite 1-jun-1999 12:00 AM

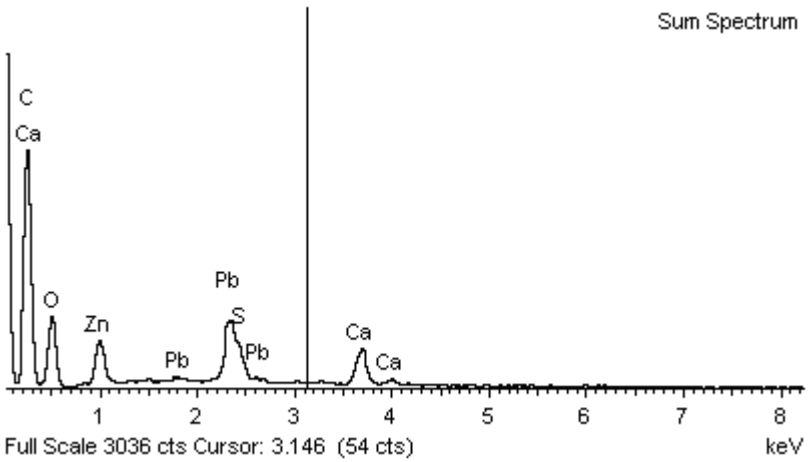
Zn Zn 1-jun-1999 12:00 AM

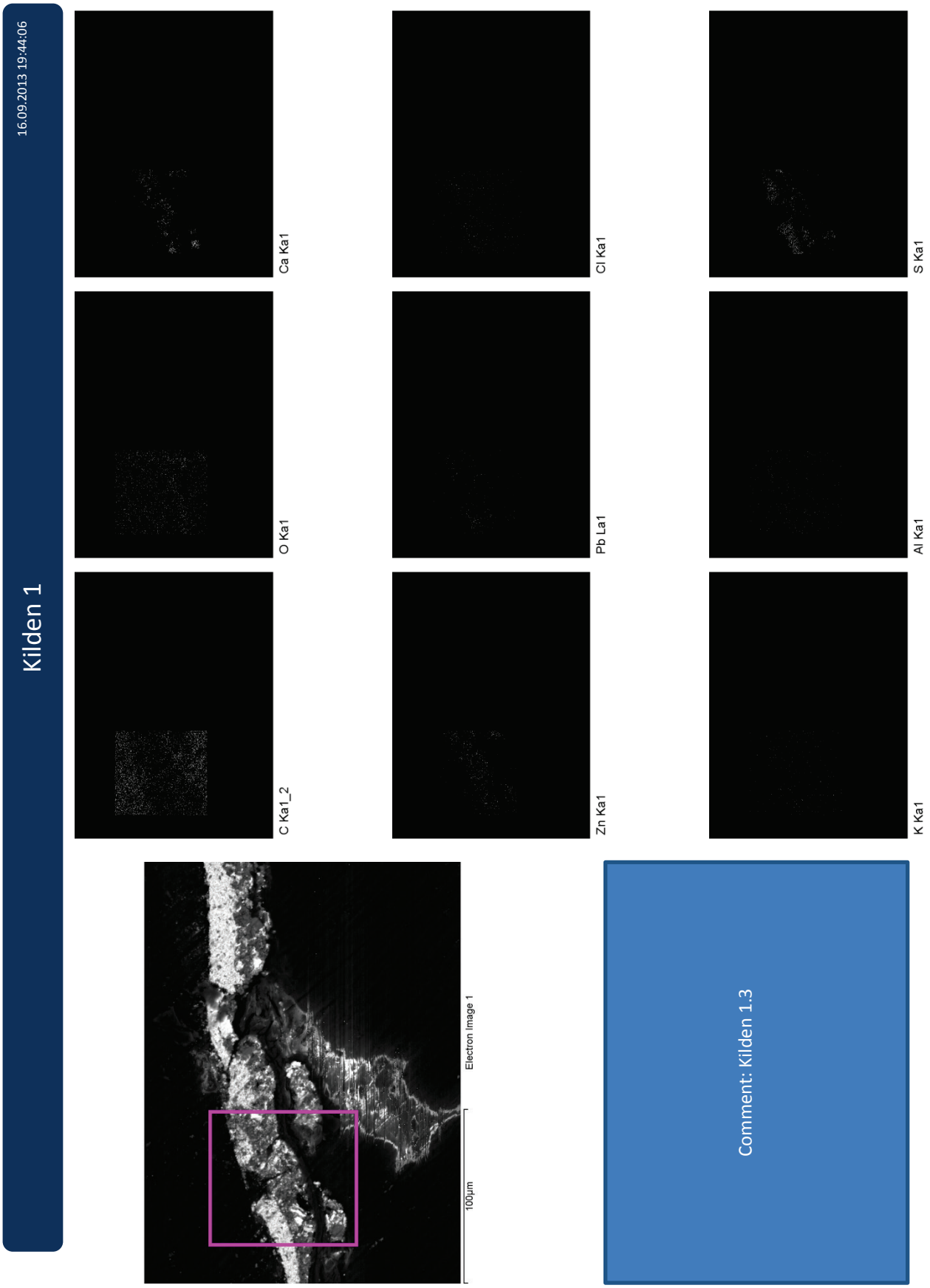
Pb PbF2 1-jun-1999 12:00 AM

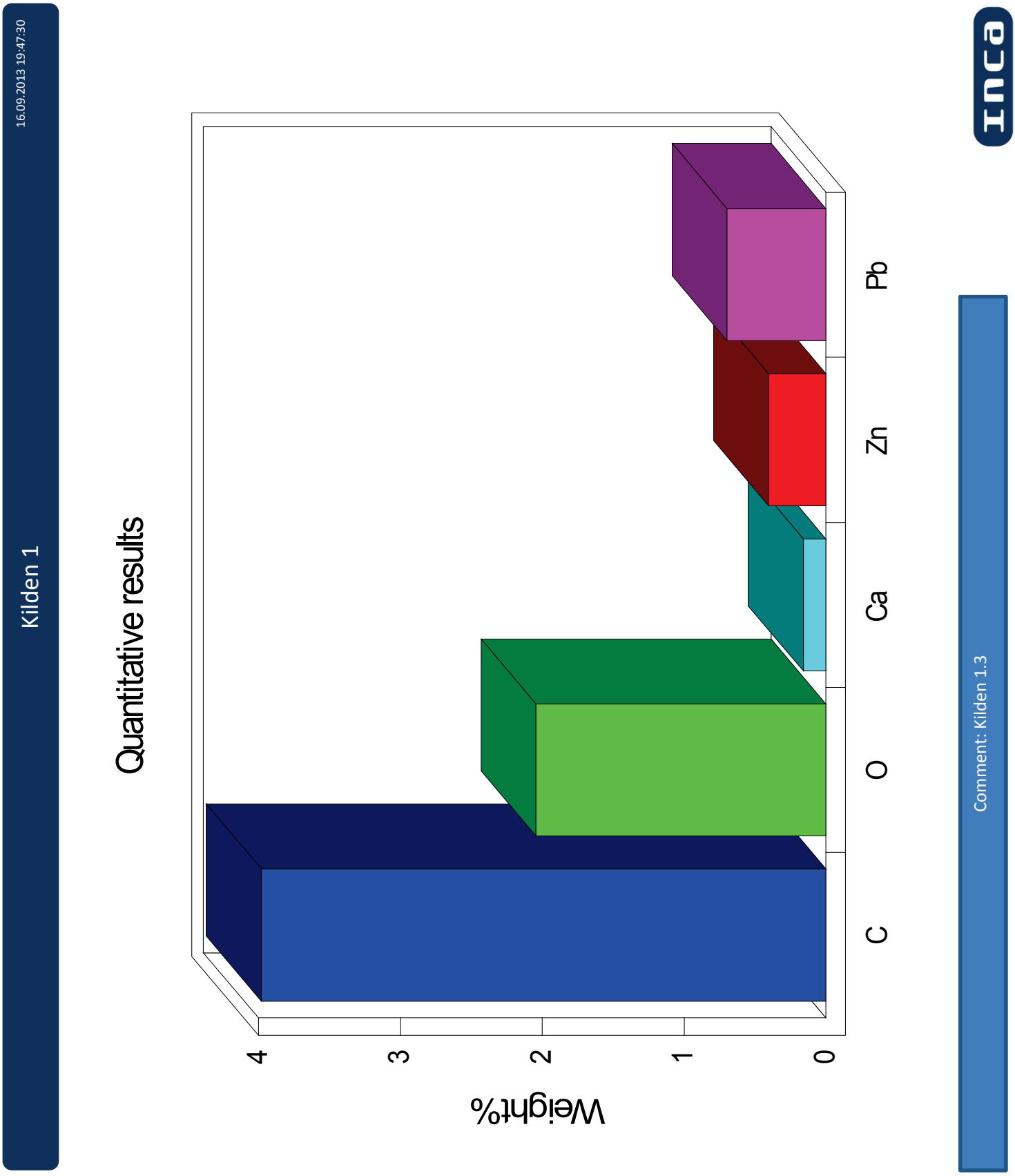
| Element | Weight% | Atomic% |
|---|---|---|
| C K | 2.39 | 69.30 |
| O K | 1.25 | 27.21 |
| S K | 0.03 | 0.30 |
| Ca K | 0.12 | 1.04 |
| Zn K | 0.30 | 1.60 |
| Pb M | 0.33 | 0.56 |
| Totals | 4.42 | |

Comment: Kilden 1.2




Kilden 1
16.09.2013 19:44:06
C Ka1_2
O Ka1
Ca Ka1
Zn Ka1
Pb La1
Cl Ka1
K Ka1
Al Ka1
S Ka1
Electron Image 1
100µm
Comment: Kilden 1.3
inca


16.09.2013 19:47:30
Kilden 1
Quantitative results
Weight%
0
1
2
3
4
C
O
Ca
Zn
Pb
Comment: Kilden 1.3
Inca

# Kilden 1

16.09.2013 19:47:38

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 3

Standard :

C CaCO3 1-jun-1999 12:00 AM

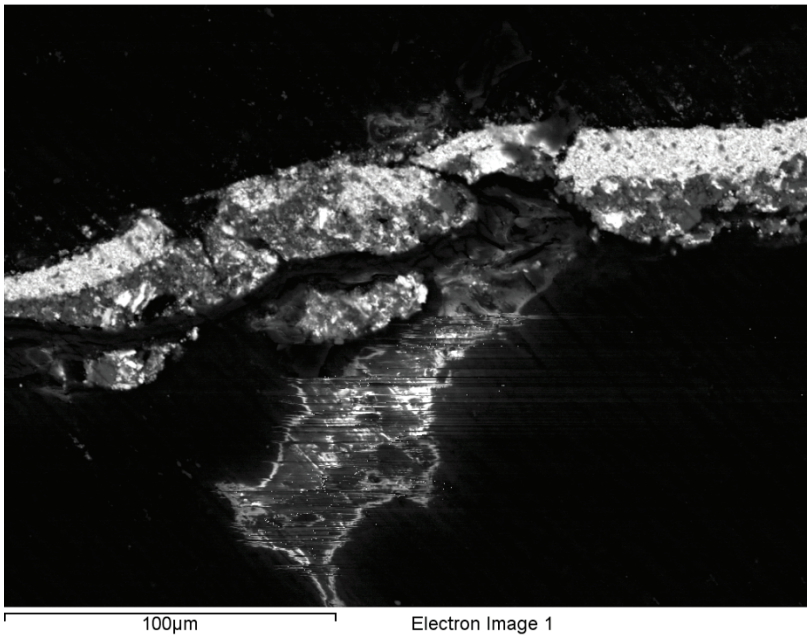
O SiO2 1-jun-1999 12:00 AM

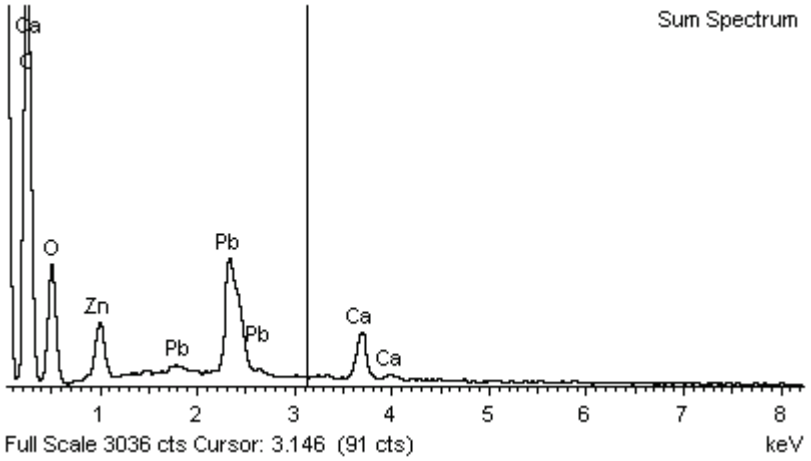
Ca Wollastonite 1-jun-1999 12:00 AM

Zn Zn 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 3.98 | 70.10 |
| O K | 2.04 | 27.02 |
| Ca K | 0.16 | 0.84 |
| Zn K | 0.41 | 1.32 |
| Pb M | 0.70 | 0.71 |
| Totals | 7.29 | |




Comment: Kilden 1.3

# Kilden 2

16.09.2013 19:08:52

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 5

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

Al Al2O3 1-jun-1999 12:00 AM

Si SiO2 1-jun-1999 12:00 AM

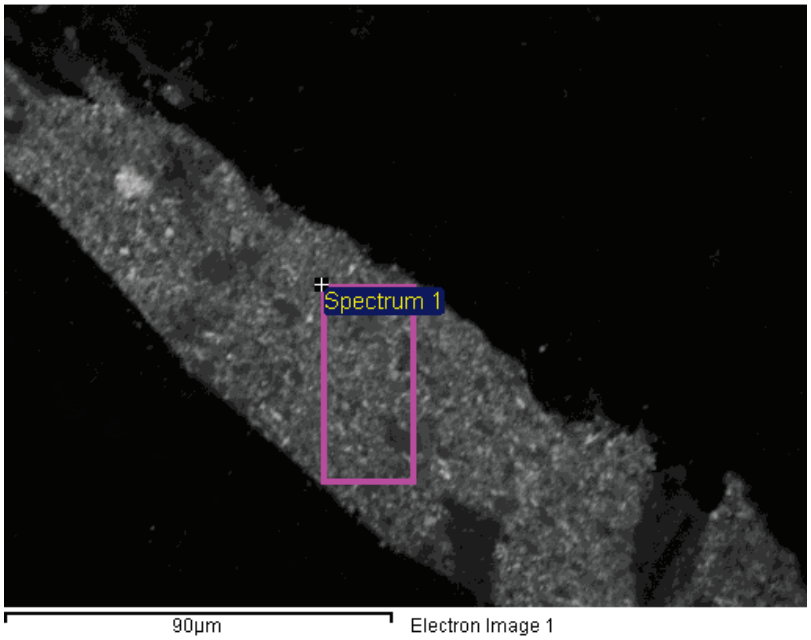
S FeS2 1-jun-1999 12:00 AM

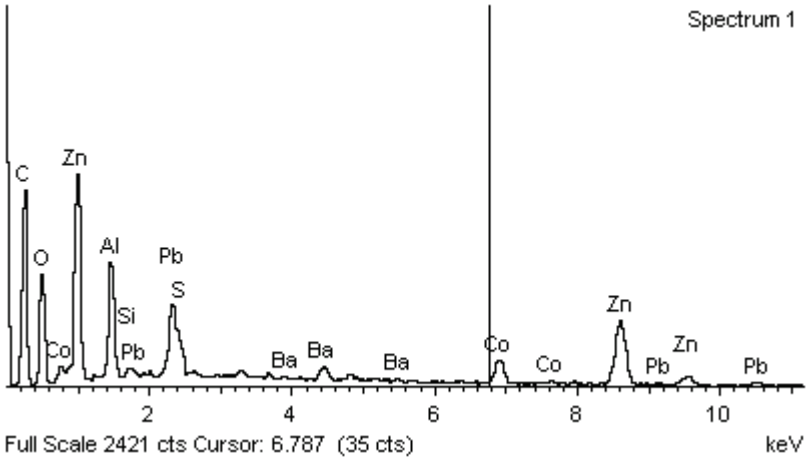
Co Co 1-jun-1999 12:00 AM

Zn Zn 1-jun-1999 12:00 AM

Ba BaF2 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM



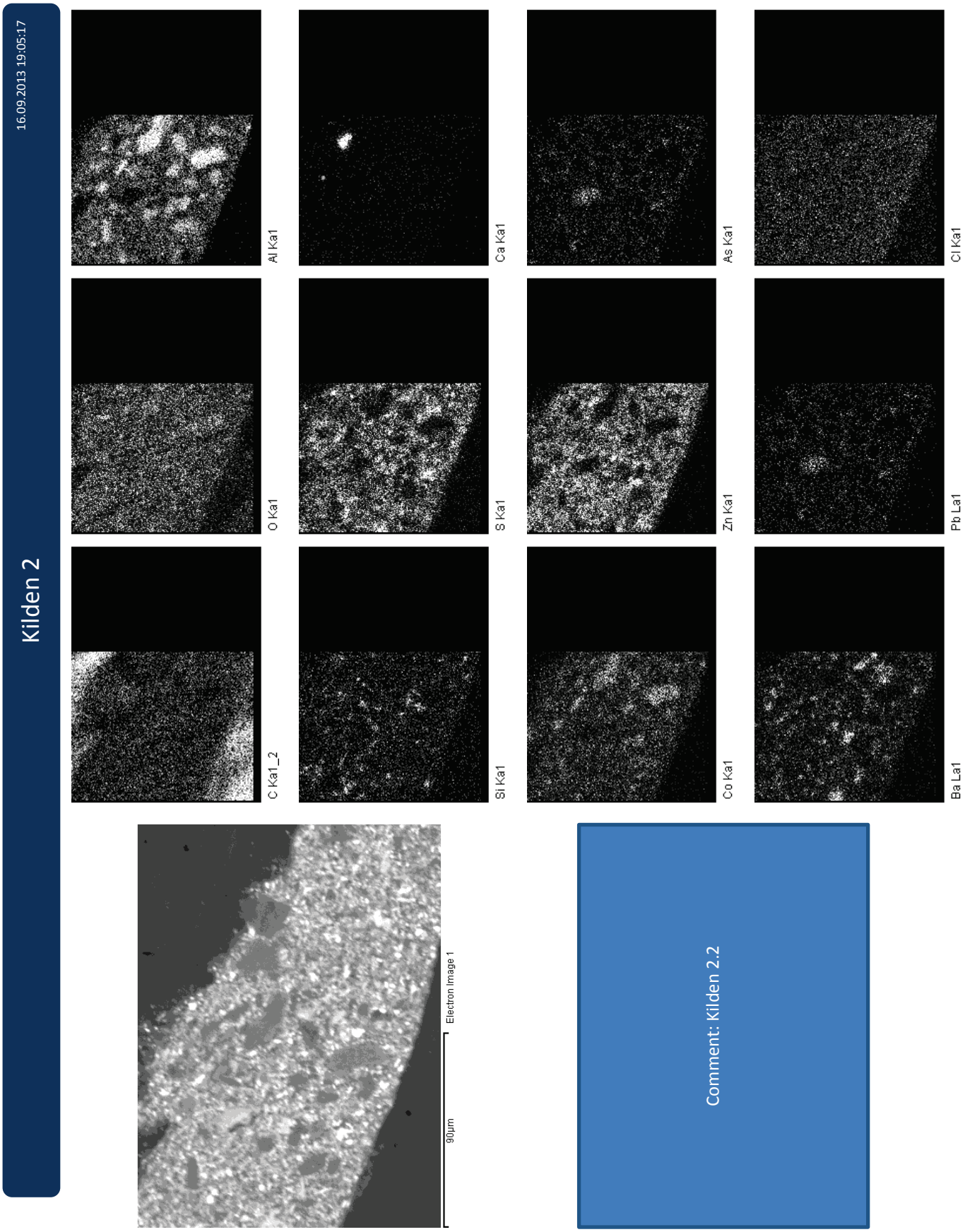



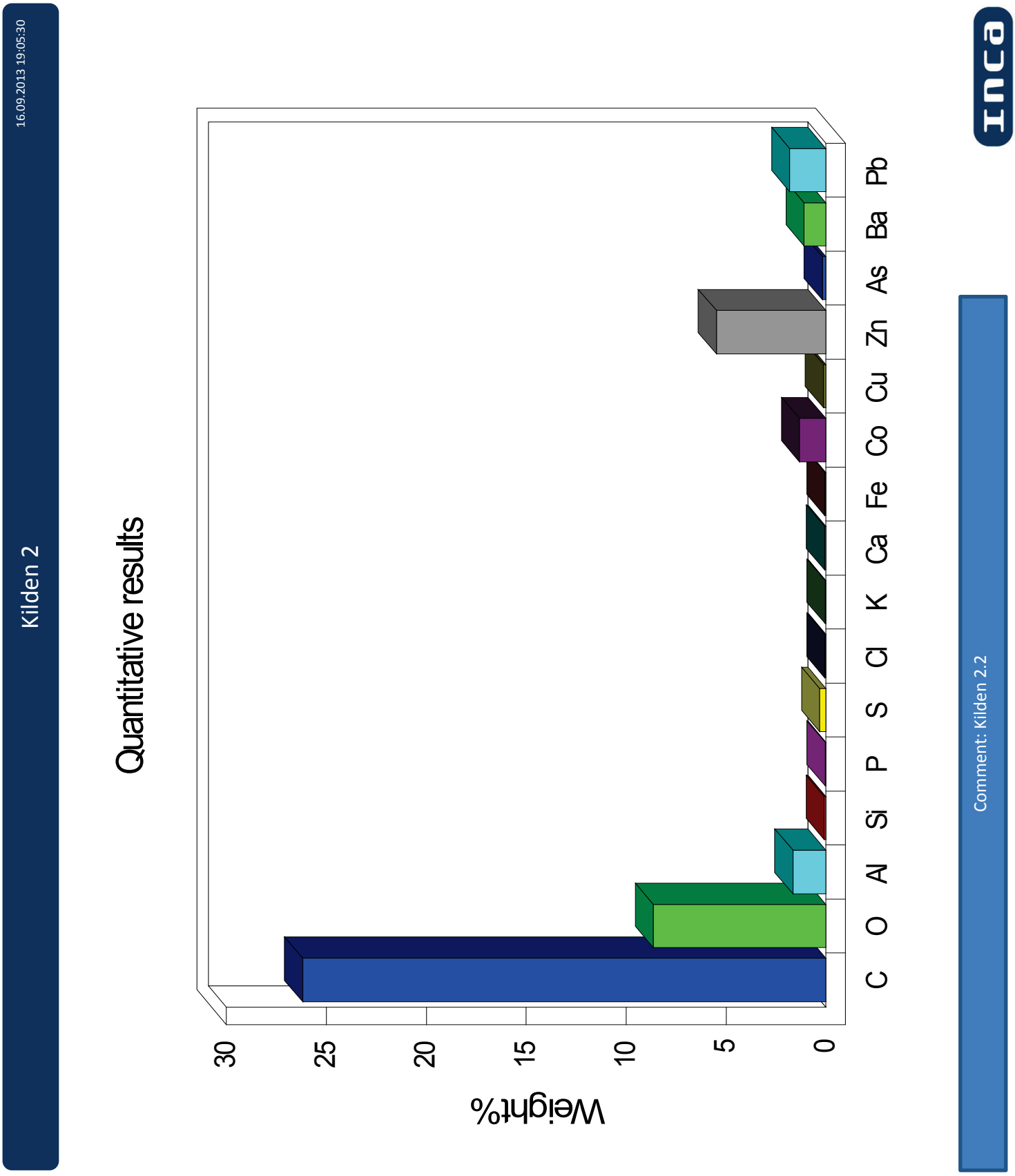

Comment: Kilden 2.1

# Kilden 2

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 29.34 | 65.30 |
| O K | 14.25 | 23.81 |
| Al K | 3.07 | 3.04 |
| Si K | 0.26 | 0.25 |
| S K | 0.37 | 0.31 |
| Co K | 2.34 | 1.06 |
| Zn K | 13.14 | 5.37 |
| Ba L | 1.61 | 0.31 |
| Pb M | 4.23 | 0.55 |
| Totals | 68.61 | |

Comment: Kilden 2.1


Kilden 2
16.09.2013 19:05:17
C Ka1_2
O Ka1
Al Ka1
Si Ka1
S Ka1
Ca Ka1
Co Ka1
Zn Ka1
As Ka1
Ba La1
Pb La1
Cl Ka1
Electron Image 1
90µm
Comment: Kilden 2.2
inca


16.09.2013 19:05:30
Kilden 2
Quantitative results
Weight%
30
25
20
15
10
5
0
C
O
Al
Si
P
S
Cl
K
Ca
Fe
Co
Cu
Zn
As
Ba
Pb
Comment: Kilden 2.2
Inca

# Kilden 2

16.09.2013 19:05:41

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 5

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

Al Al2O3 1-jun-1999 12:00 AM

Si SiO2 1-jun-1999 12:00 AM

P GaP 1-jun-1999 12:00 AM

S FeS2 1-jun-1999 12:00 AM

Cl KCl 1-jun-1999 12:00 AM

K MAD-10 Feldspar 1-jun-1999 12:00 AM

Ca Wollastonite 1-jun-1999 12:00 AM

Fe Fe 1-jun-1999 12:00 AM

Co Co 1-jun-1999 12:00 AM

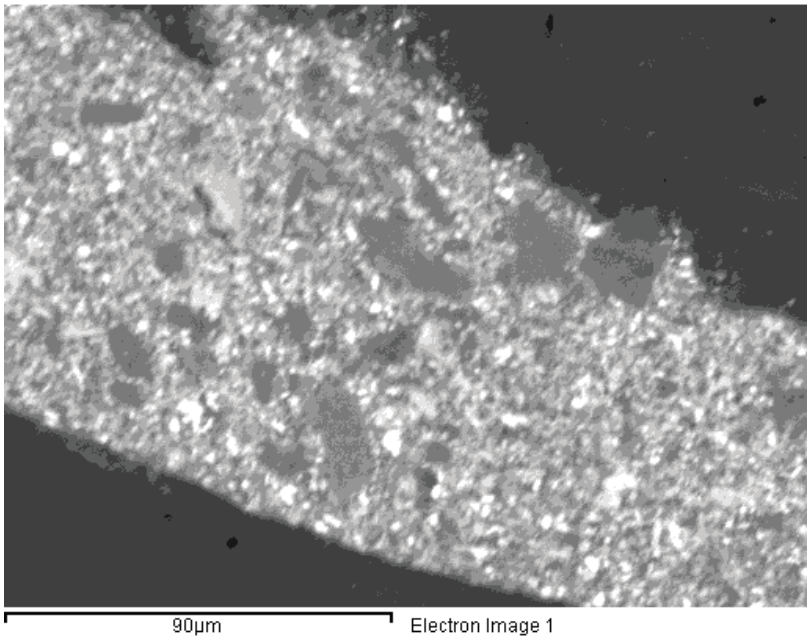
Cu Cu 1-jun-1999 12:00 AM

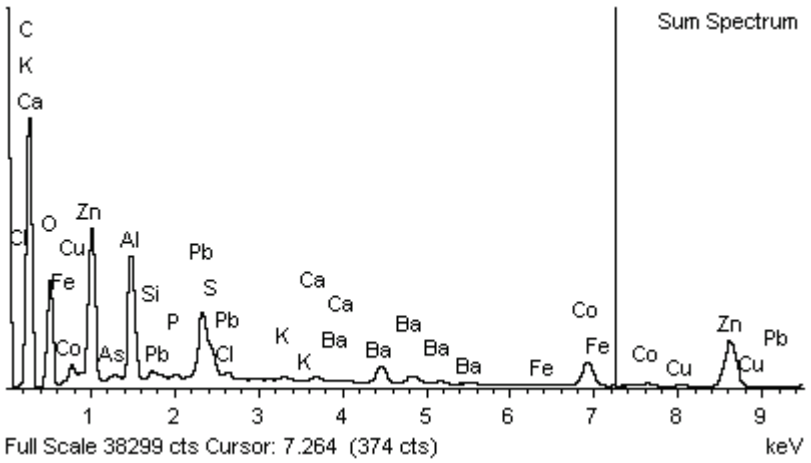
Zn Zn 1-jun-1999 12:00 AM

As InAs 1-jun-1999 12:00 AM

Ba BaF2 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM



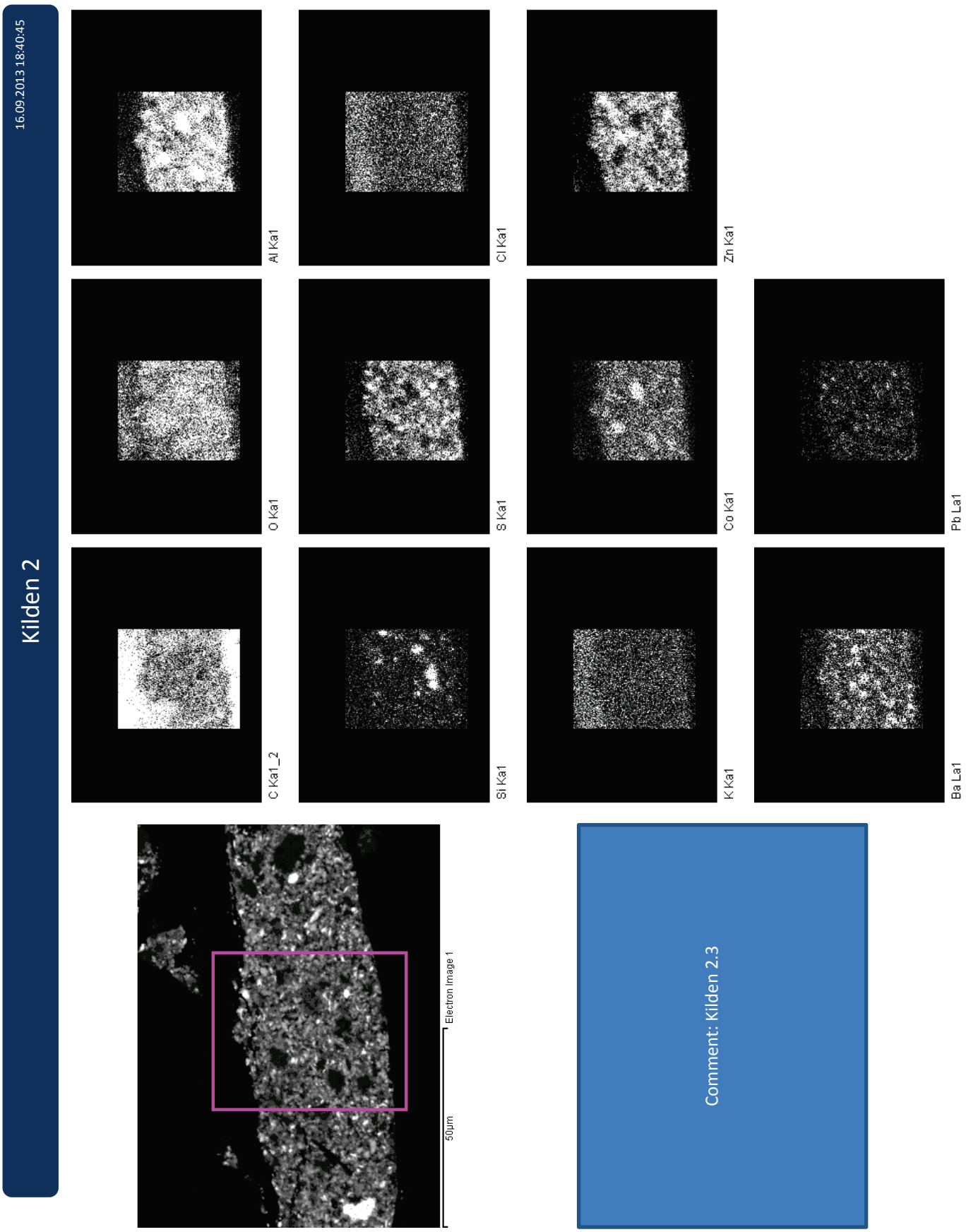



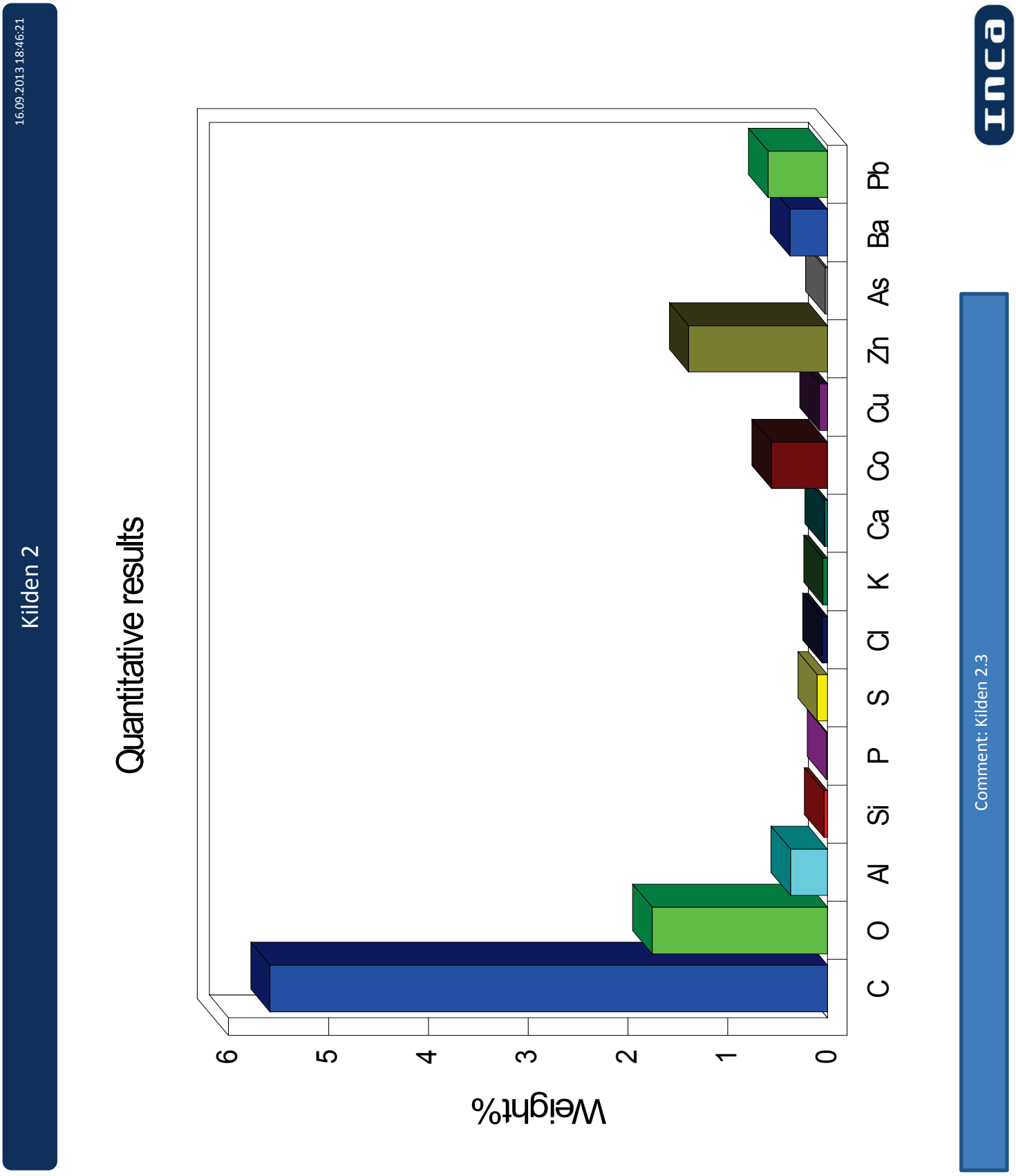

Comment: Kilden 2.2

## Kilden 2

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 26.19 | 74.36 |
| O K | 8.65 | 18.44 |
| Al K | 1.66 | 2.10 |
| Si K | 0.09 | 0.11 |
| P K | 0.05 | 0.06 |
| S K | 0.33 | 0.35 |
| Cl K | 0.07 | 0.07 |
| K K | 0.05 | 0.05 |
| Ca K | 0.08 | 0.07 |
| Fe K | 0.05 | 0.03 |
| Co K | 1.33 | 0.77 |
| Cu K | 0.14 | 0.07 |
| Zn K | 5.49 | 2.86 |
| As L | 0.20 | 0.09 |
| Ba L | 1.11 | 0.28 |
| Pb M | 1.82 | 0.30 |
| Totals | 47.32 | |

Comment: Kilden 2.2


16.09.2013 18:40:45
Kilden 2
Al Ka1
Cl Ka1
Zn Ka1
O Ka1
S Ka1
Co Ka1
Pb La1
C Ka1_2
Si Ka1
K Ka1
Ba La1
Electron Image 1
50µm
Comment: Kilden 2.3
inca


16.09.2013 18:46:21
Kilden 2
Quantitative results
Weight%
0
1
2
3
4
5
6
C
O
Al
Si
P
S
Cl
K
Ca
Co
Cu
Zn
As
Ba
Pb
inca
Comment: Kilden 2.3

# Kilden 2

16.09.2013 18:47:12

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 4

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

Al Al2O3 1-jun-1999 12:00 AM

Si SiO2 1-jun-1999 12:00 AM

P GaP 1-jun-1999 12:00 AM

S FeS2 1-jun-1999 12:00 AM

Cl KCl 1-jun-1999 12:00 AM

K MAD-10 Feldspar 1-jun-1999 12:00 AM

Ca Wollastonite 1-jun-1999 12:00 AM

Co Co 1-jun-1999 12:00 AM

Cu Cu 1-jun-1999 12:00 AM

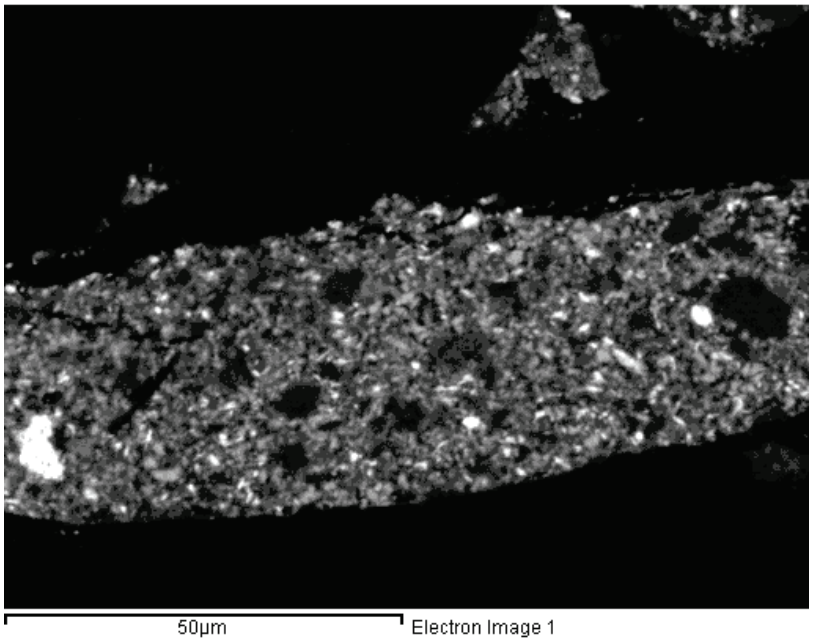
Zn Zn 1-jun-1999 12:00 AM

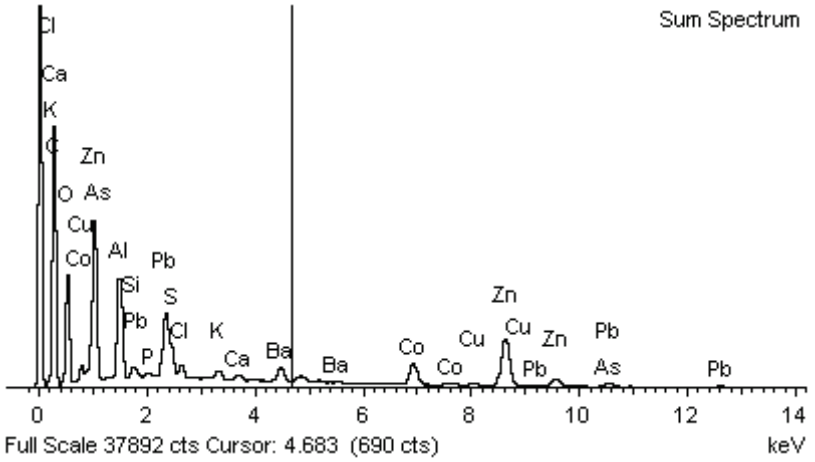
As InAs 1-jun-1999 12:00 AM

Ba BaF2 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM

Comment: Kilden 2.3

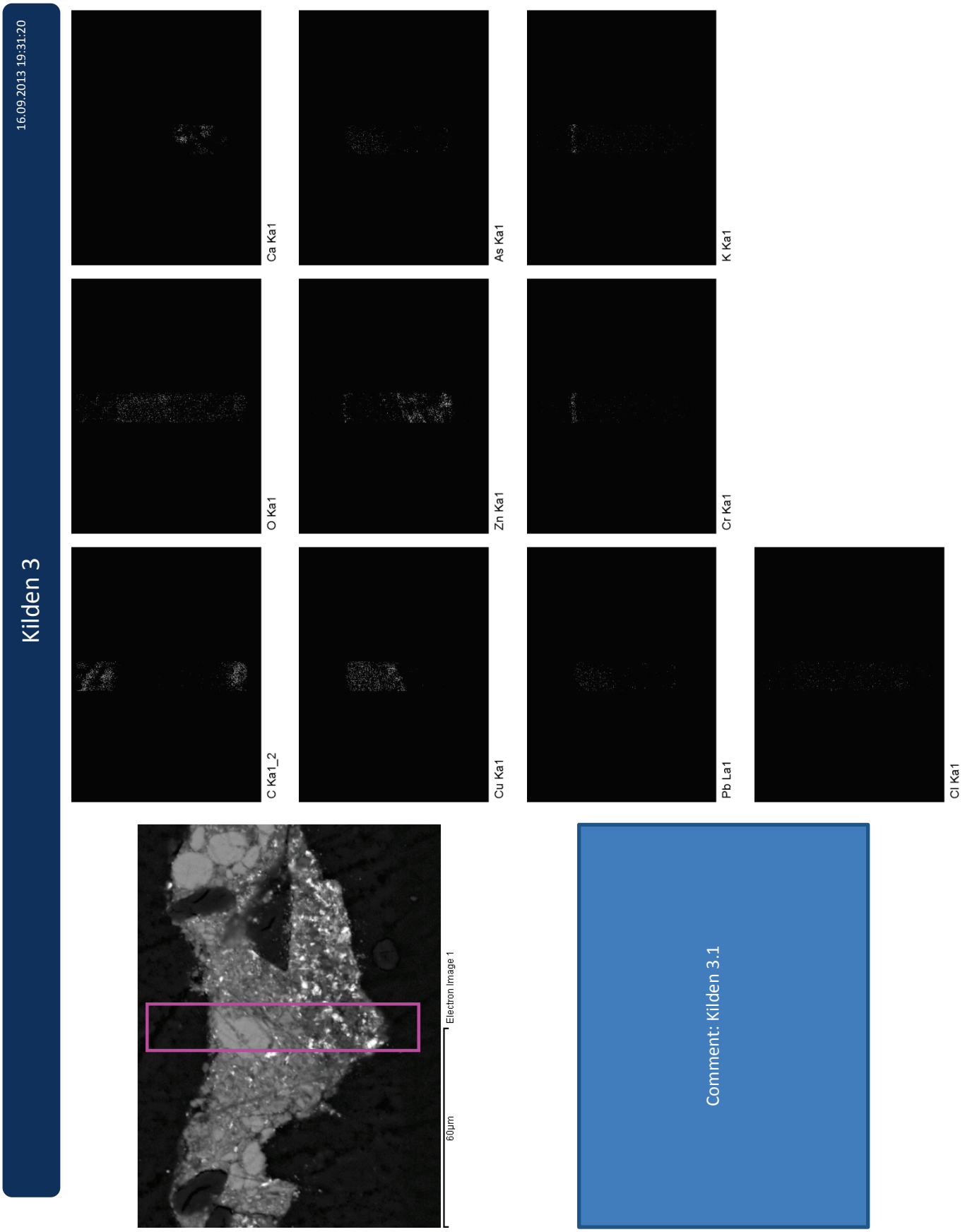


## Kilden 2

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 5.59 | 73.17 |
| O K | 1.76 | 17.29 |
| Al K | 0.37 | 2.18 |
| Si K | 0.04 | 0.22 |
| P K | 0.01 | 0.06 |
| S K | 0.10 | 0.51 |
| Cl K | 0.05 | 0.24 |
| K K | 0.05 | 0.19 |
| Ca K | 0.03 | 0.13 |
| Co K | 0.56 | 1.50 |
| Cu K | 0.09 | 0.21 |
| Zn L | 1.39 | 3.35 |
| As L | 0.03 | 0.06 |
| Ba L | 0.38 | 0.43 |
| Pb M | 0.60 | 0.45 |
| Totals | 11.05 | |

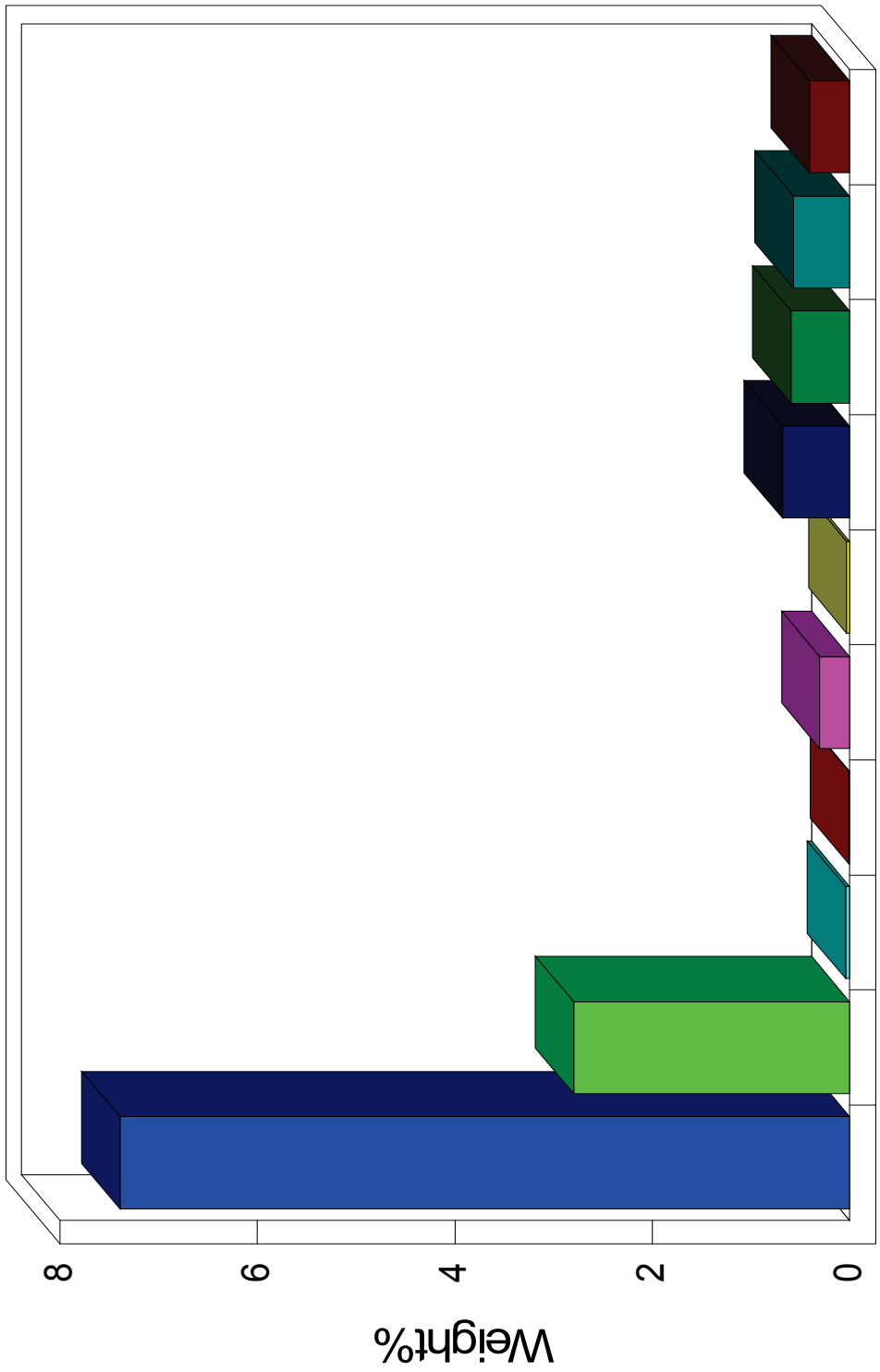
Comment: Kilden 2.3


16.09.2013 19:31:20
Kilden 3
Ca Ka1
As Ka1
K Ka1
O Ka1
Zn Ka1
Cr Ka1
C Ka1_2
Cu Ka1
Pb La1
Cl Ka1
Electron Image 1
60µm
Comment: Kilden 3.1
inca

16.09.2013 19:31:34

Kilden 3

Quantitative results




Comment: Kilden 3.1

# Kilden 3

16.09.2013 19:31:47

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 3

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

S FeS2 1-jun-1999 12:00 AM

K MAD-10 Feldspar 1-jun-1999 12:00 AM

Ca Wollastonite 1-jun-1999 12:00 AM

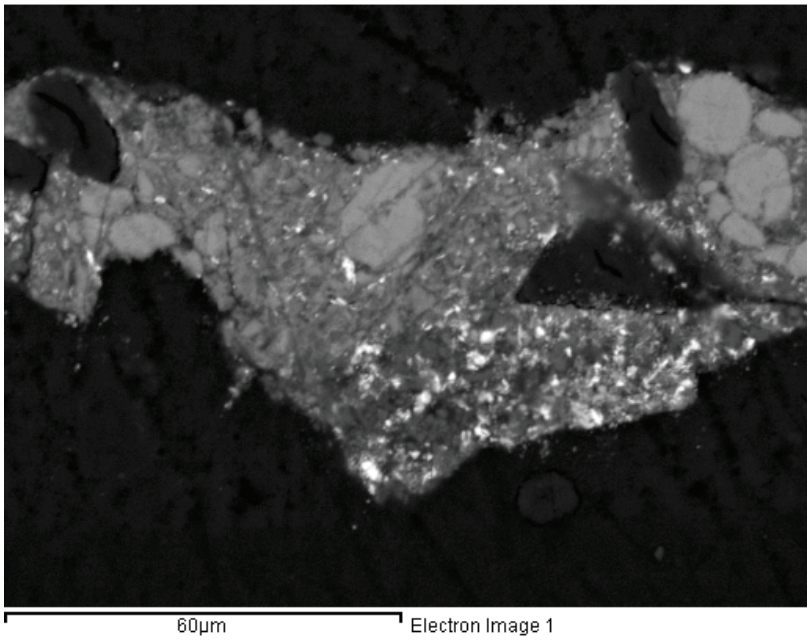
Cr Cr 1-jun-1999 12:00 AM

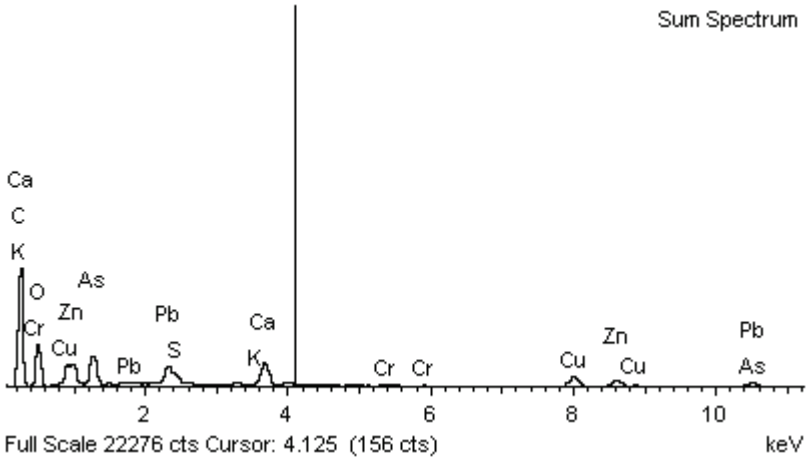
Cu Cu 1-jun-1999 12:00 AM

Zn Zn 1-jun-1999 12:00 AM

As InAs 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM



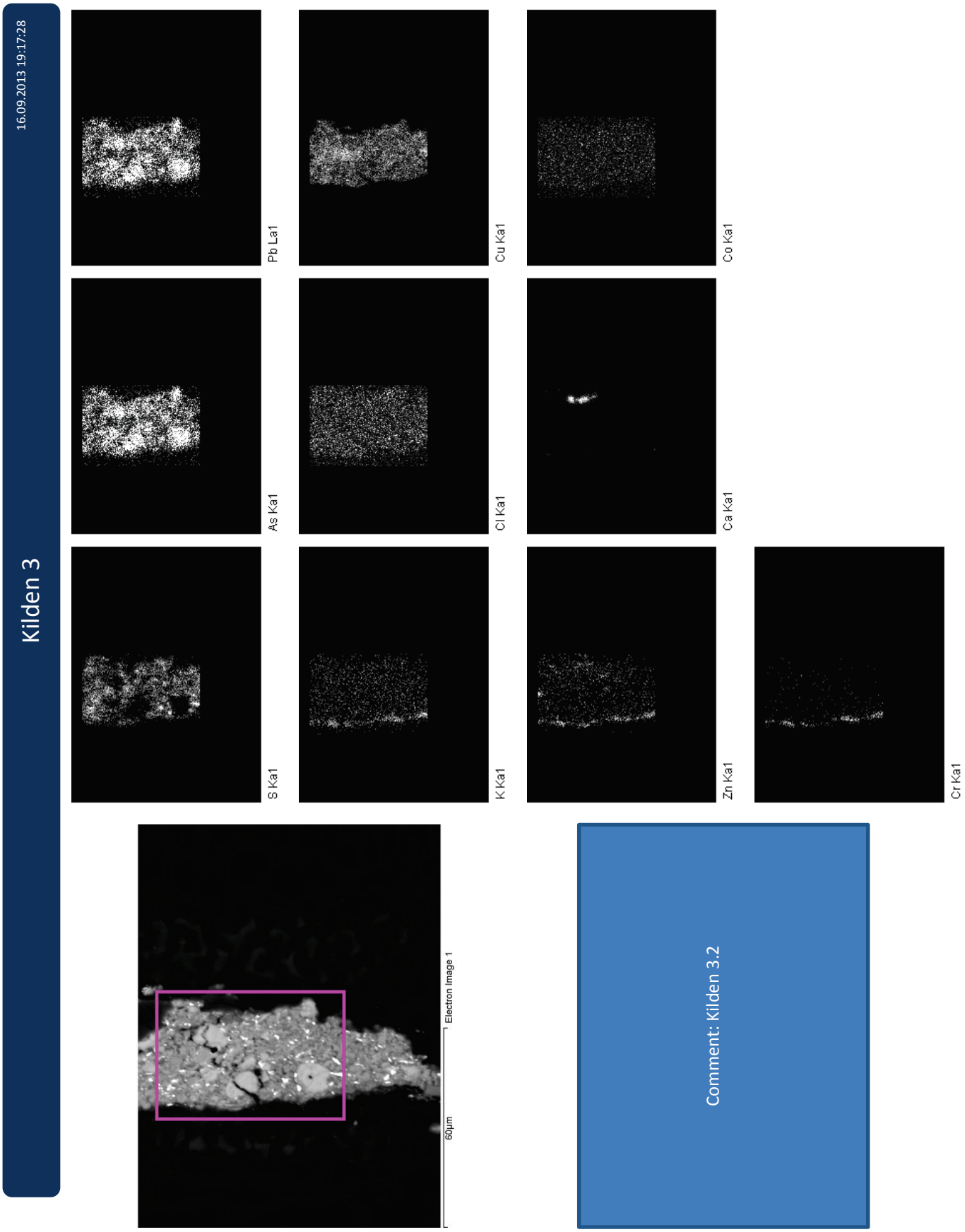




Comment: Kilden 3.1

## Kilden 3

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 7.39 | 74.17 |
| O K | 2.80 | 21.08 |
| S K | 0.04 | 0.16 |
| K K | 0.01 | 0.04 |
| Ca K | 0.30 | 0.91 |
| Cr K | 0.03 | 0.07 |
| Cu K | 0.68 | 1.29 |
| Zn K | 0.60 | 1.10 |
| As L | 0.58 | 0.93 |
| Pb M | 0.41 | 0.24 |
| Totals | 12.85 | |

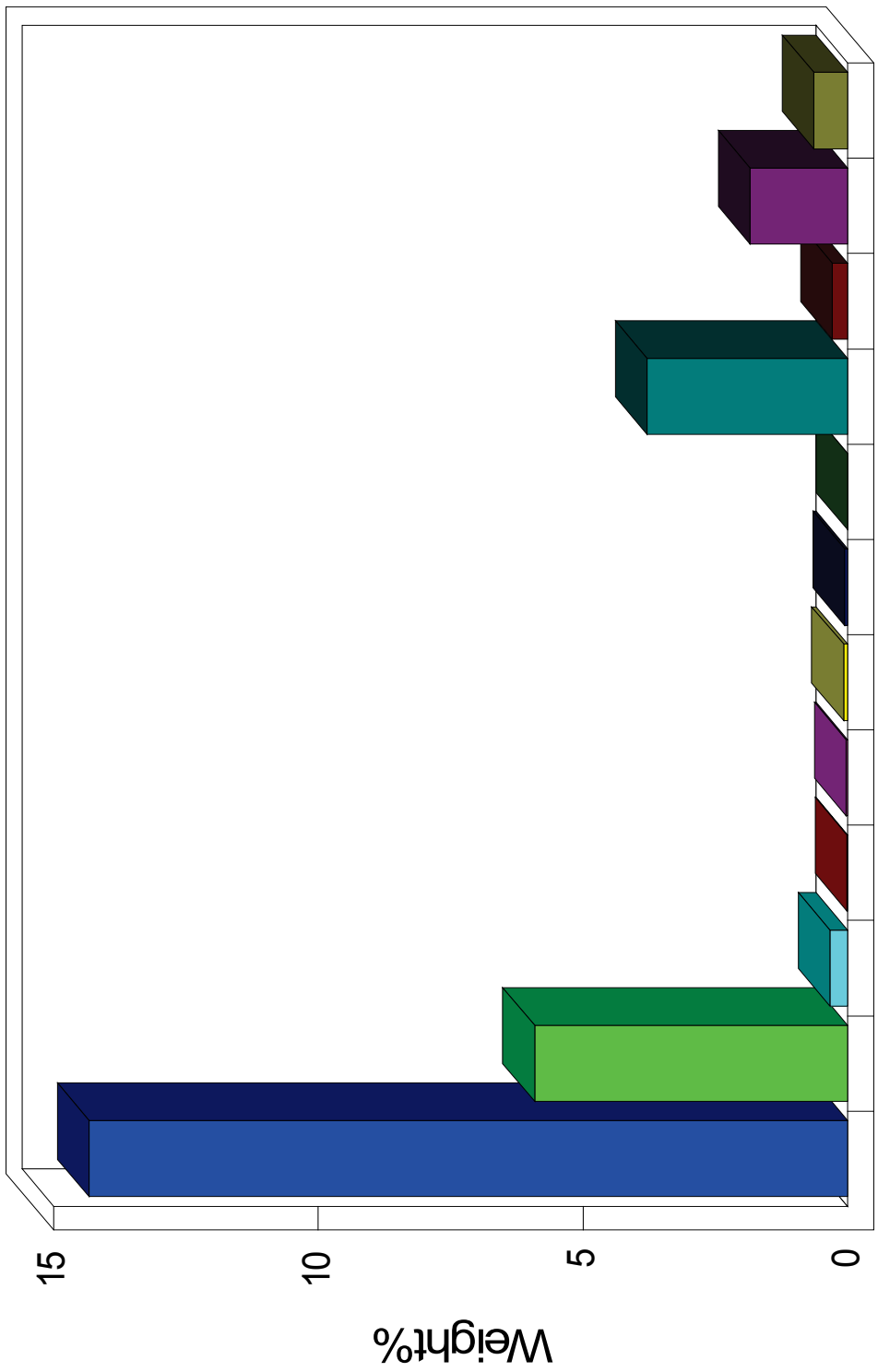
Comment: Kilden 3.1


16.09.2013 19:17:28
Kilden 3
Pb La1
Cu Ka1
Co Ka1
As Ka1
Cl Ka1
Ca Ka1
S Ka1
K Ka1
Zn Ka1
Cr Ka1
Electron Image 1
60µm
Comment: Kilden 3.2
inca

16.09.2013 19:17:49

Kilden 3

Quantitative results




Comment: Kilden 3.2

# Kilden 3

16.09.2013 19:18:12

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 5

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

S FeS2 1-jun-1999 12:00 AM

Cl KCl 1-jun-1999 12:00 AM

K MAD-10 Feldspar 1-jun-1999 12:00 AM

Ca Wollastonite 1-jun-1999 12:00 AM

Cr Cr 1-jun-1999 12:00 AM

Co Co 1-jun-1999 12:00 AM

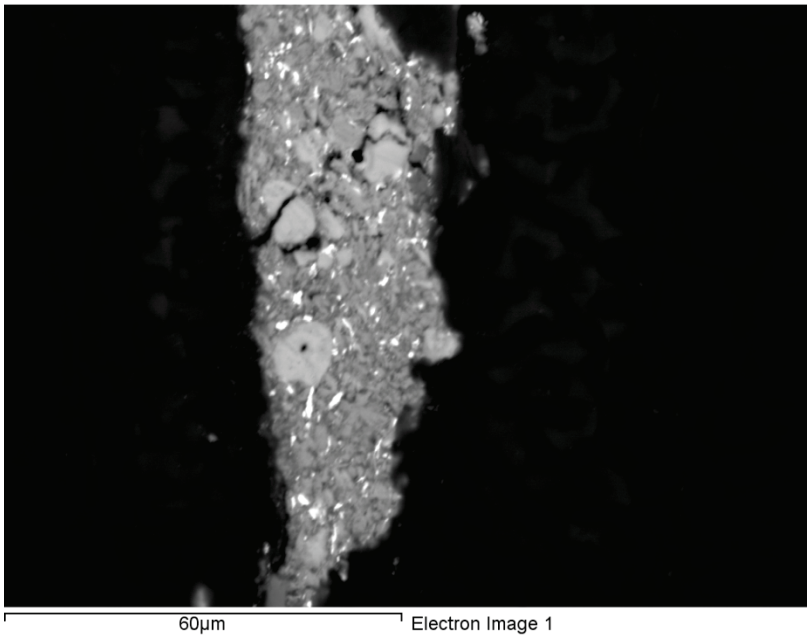
Cu Cu 1-jun-1999 12:00 AM

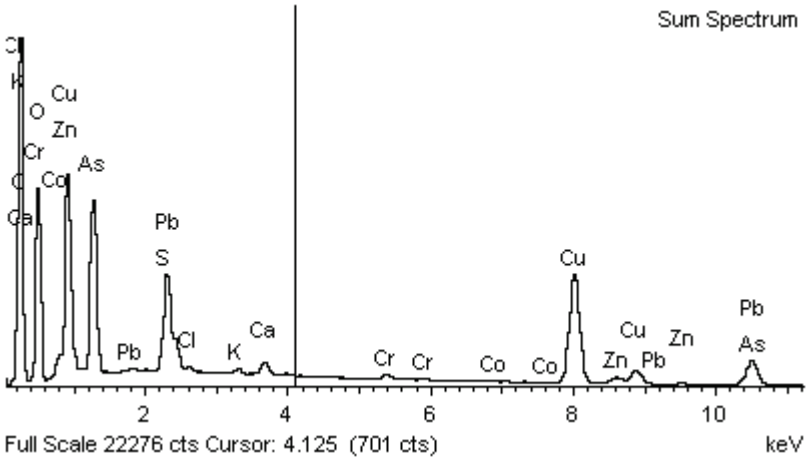
Zn Zn 1-jun-1999 12:00 AM

As InAs 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM

Comment: Kilden 3.2

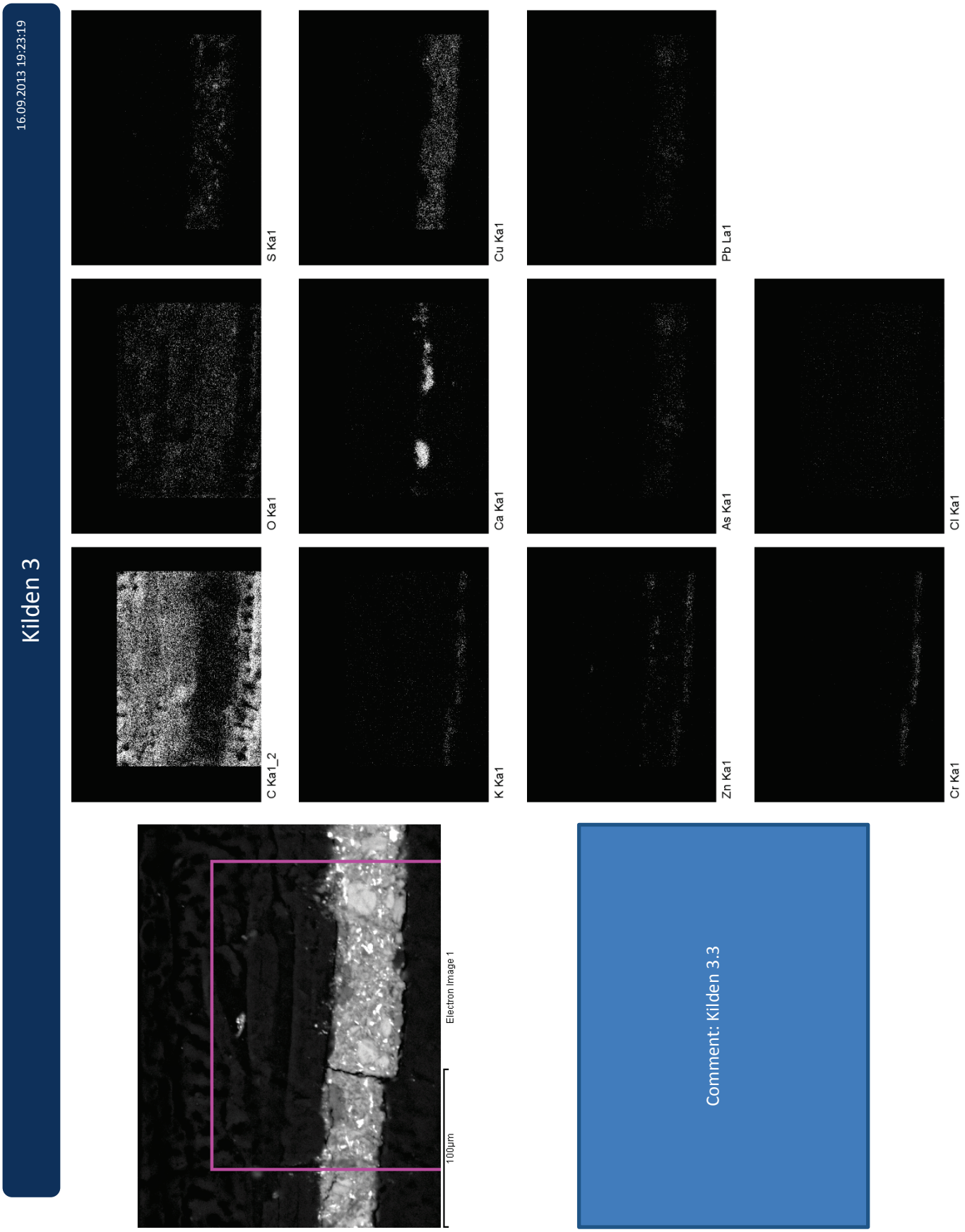


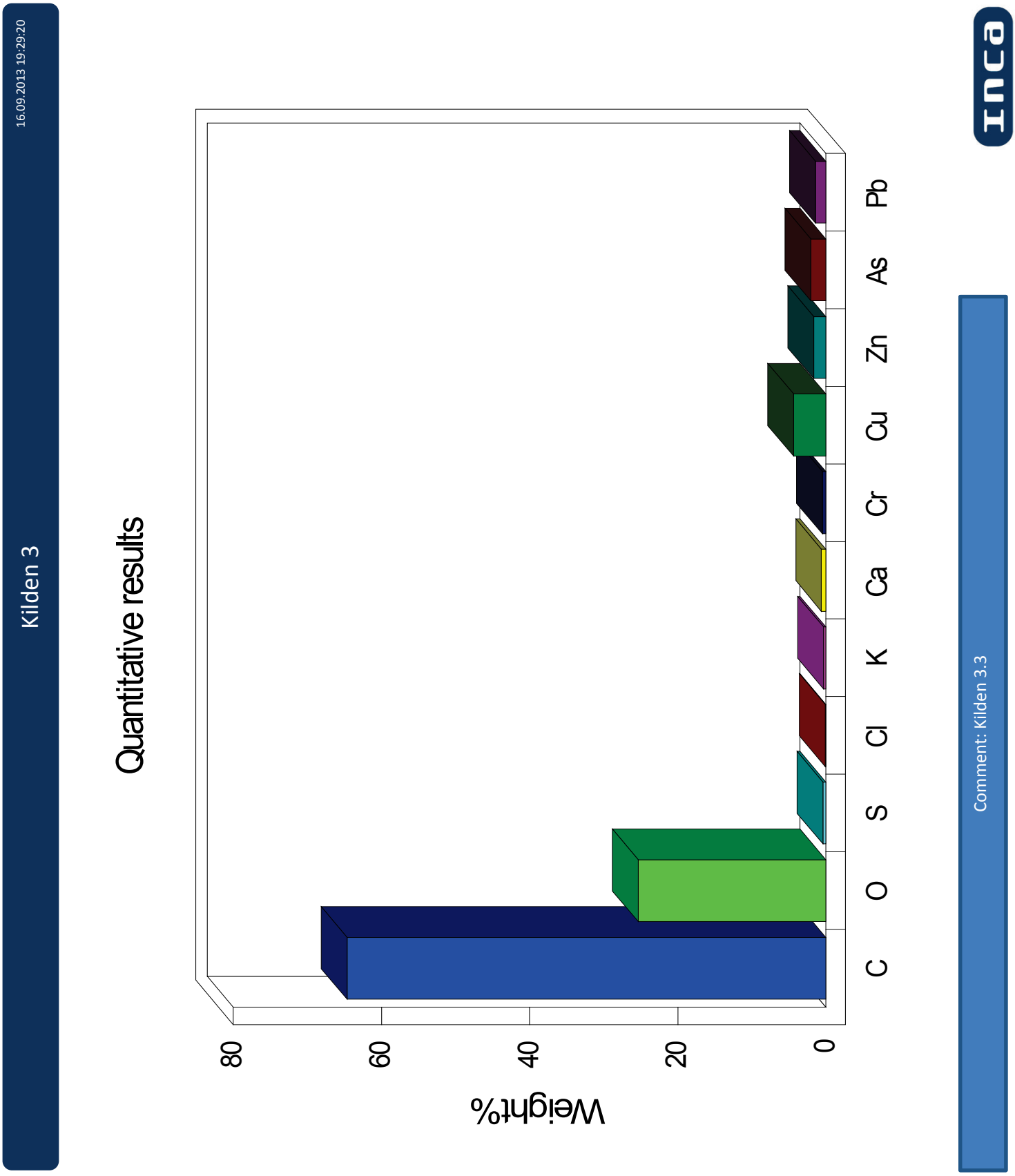



## Kilden 3

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 14.33 | 71.45 |
| O K | 5.92 | 22.15 |
| S K | 0.34 | 0.63 |
| Cl K | 0.01 | 0.02 |
| K K | 0.03 | 0.04 |
| Ca K | 0.08 | 0.12 |
| Cr K | 0.06 | 0.07 |
| Co K | 0.00 | 0.00 |
| Cu K | 3.79 | 3.58 |
| Zn K | 0.29 | 0.26 |
| As L | 1.85 | 1.48 |
| Pb M | 0.65 | 0.19 |
| Totals | 27.35 | |

Comment: Kilden 3.2


16.09.2013 19:23:19
Kilden 3
S Ka1
Cu Ka1
Pb La1
O Ka1
Ca Ka1
As Ka1
Cl Ka1
C Ka1_2
K Ka1
Zn Ka1
Cr Ka1
Electron Image 1
100µm
Comment: Kilden 3.3
inca


16.09.2013 19:29:20
Kilden 3
Quantitative results
Weight%
0
20
40
60
80
C
O
S
Cl
K
Ca
Cr
Cu
Zn
As
Pb
inca
Comment: Kilden 3.3

# Kilden 3

16.09.2013 19:29:33

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed

Number of iterations = 5

Standard :

C CaCO3 1-jun-1999 12:00 AM

O SiO2 1-jun-1999 12:00 AM

S FeS2 1-jun-1999 12:00 AM

Cl KCl 1-jun-1999 12:00 AM

K MAD-10 Feldspar 1-jun-1999 12:00 AM

Ca Wollastonite 1-jun-1999 12:00 AM

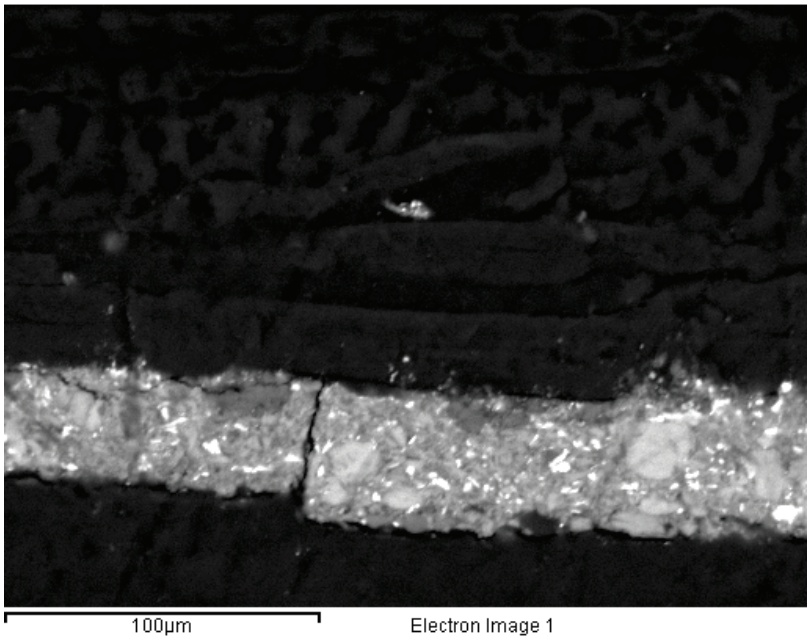
Cr Cr 1-jun-1999 12:00 AM

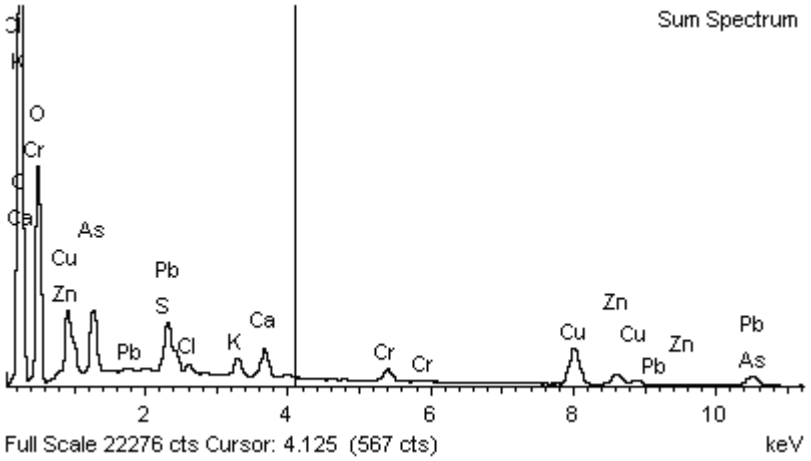
Cu Cu 1-jun-1999 12:00 AM

Zn Zn 1-jun-1999 12:00 AM

As InAs 1-jun-1999 12:00 AM

Pb PbF2 1-jun-1999 12:00 AM




Comment: Kilden 3.3

# Kilden 3

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 64.65 | 75.32 |
| O K | 25.35 | 22.17 |
| S K | 0.39 | 0.17 |
| Cl K | 0.13 | 0.05 |
| K K | 0.36 | 0.13 |
| Ca K | 0.61 | 0.21 |
| Cr K | 0.52 | 0.14 |
| Cu K | 4.40 | 0.97 |
| Zn K | 1.66 | 0.36 |
| As L | 2.04 | 0.38 |
| Pb M | 1.44 | 0.10 |
| Totals | 101.55 | |

Comment: Kilden 3.3

# APPENDIX 2: OPERATING DATA ON XRF MEASUREMENTS, INCLUDING SELECTED SPECTRAS ON TRANSECT NO. 1

## Kilden tidemarks – ED pXRF analysis

Painting analysed accross a series of transects covering the tide mark, at different locations on the canvas.

Transects

| Number | Location |
|---|---|
| 1 | Light blue (sky) |
| 2 | Blue (mountain) |
| 3 | Green (landscape) |
| 4 | Light red (flesh) |
| 5 | White/ ground (heel) |
| 6 | Light purple (water) |
| 7 | Ground |

Sample points per transect

| Number | Location |
|---|---|
| 1 | left side outside tide mark (Blue) |
| 2 | border region to left of tide mark (orange) |
| 3 | Tide mark (red) |
| 4 | Border region to right of tide mark (pink) |
| 5 | Right side outside the tide mark (green) |

| Sample | Time (s) | Transect | Location | Description |
|---|---|---|---|---|
| 23 | 121,6 | 1 | 1 | Lys blaa |
| 24 | 120,94 | 1 | 2 | Lys blaa, randsone v |
| 25 | 121 | 1 | 3 | Lys blaa, midt |
| 26 | 121,12 | 1 | 4 | Lys blaa, randsone h |
| 28 | 121,14 | 1 | 5 | Lys blaa |
| 29 | 121,27 | 2 | 1 | Blaa |
| 30 | 120,99 | 2 | 2 | Blaa, randsone v |
| 31 | 121,09 | 2 | 3 | Blaa, midt |
| 32 | 121,08 | 2 | 4 | Blaa, randsone h |
| 33 | 120,81 | 2 | 5 | Blaa |

| | | | | |
|---|---|---|---|---|
| 34 | 120,77 | 3 | 1 | Gronn |
| 35 | 120,89 | 3 | 2 | Gronn, randsone v |
| 36 | 120,8 | 3 | 3 | Gronn, midt |
| 37 | 120,86 | 3 | 4 | Gronn, randsone h |
| 38 | 120,78 | 3 | 5 | Gronn |
| 39 | 120,31 | 4a | 3 | Rod, hud, midt |
| 40 | 120,93 | 4a | 4 | Rod, hud, randsone |
| 41 | 120,85 | 4a | 5 | Rod, hud |
| 42 | 120,48 | 4b | 1 | Rod, hud |
| 43 | 121,51 | 4b | 2 | Rod, hud, randsone |
| 44 | 120,72 | 4b | 3 | Rod, hud, midt |
| 45 | 121,41 | 5 | 1 | Grundering |
| 46 | 120,45 | 5 | 2 | Grundering, randsone v |
| 47 | 120,26 | 5 | 3 | Grundering, midt |
| 48 | 120,74 | 5 | 4 | Grundering, randsone h |
| 49 | 120,85 | 5 | 5 | Grundering |
| 50 | 120,82 | 6 | 1 | Lys fiolett |
| 51 | 120,44 | 6 | 2 | Lys fiolett, randsone |
| 52 | 120,55 | 6 | 3 | Lys fiolett, midt |
| 53 | 120,44 | 6 | 4 | Lys fiolett, randsone h |
| 54 | 120,65 | 6 | 5 | Lys fiolett |
| 55 | 121,16 | 7 | | Bar grundering |

Niton XL3t pXRF with GOLDD+ silicone drift detector (higher count rate than previous pin diode detector technology), Mining mode

Each XRF analysis done in 4 ranges (30s per range):

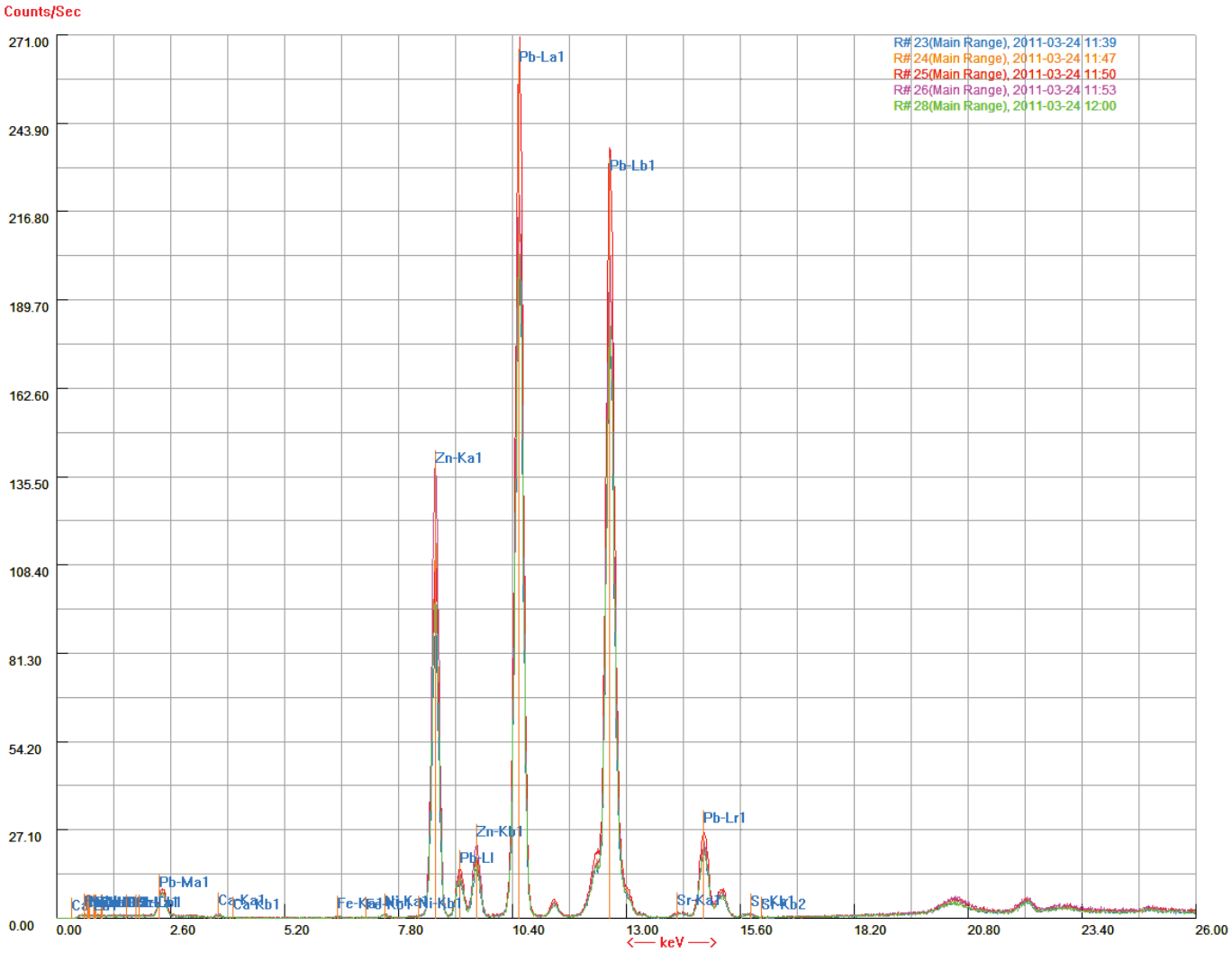
| **Range** | **Different modes (using different voltage (kV), current (µA), and filters to target different elements)** | **Voltage (kV)** | **Current (uA)*** |
|---|---|---|---|
| Main | Mn – Bi (can see Ti, V, Cr and lighter elements but not as sensitive as low or light ranges) | 50 | Upto 40 |
| High | Ba to Ag, | 50 | Upto 40 |
| Low | K – Cr | 20 | Upto 100 |
| Light | Light element analysis (e,g, Mg-Cl) | 8 | Upto 199 |

*Automatically selected by the analyser - higher dead time, lower current

**Selected spectra**

## Transect 1

Main range, Main elements identified: Zn, Pb, Sr, Ca



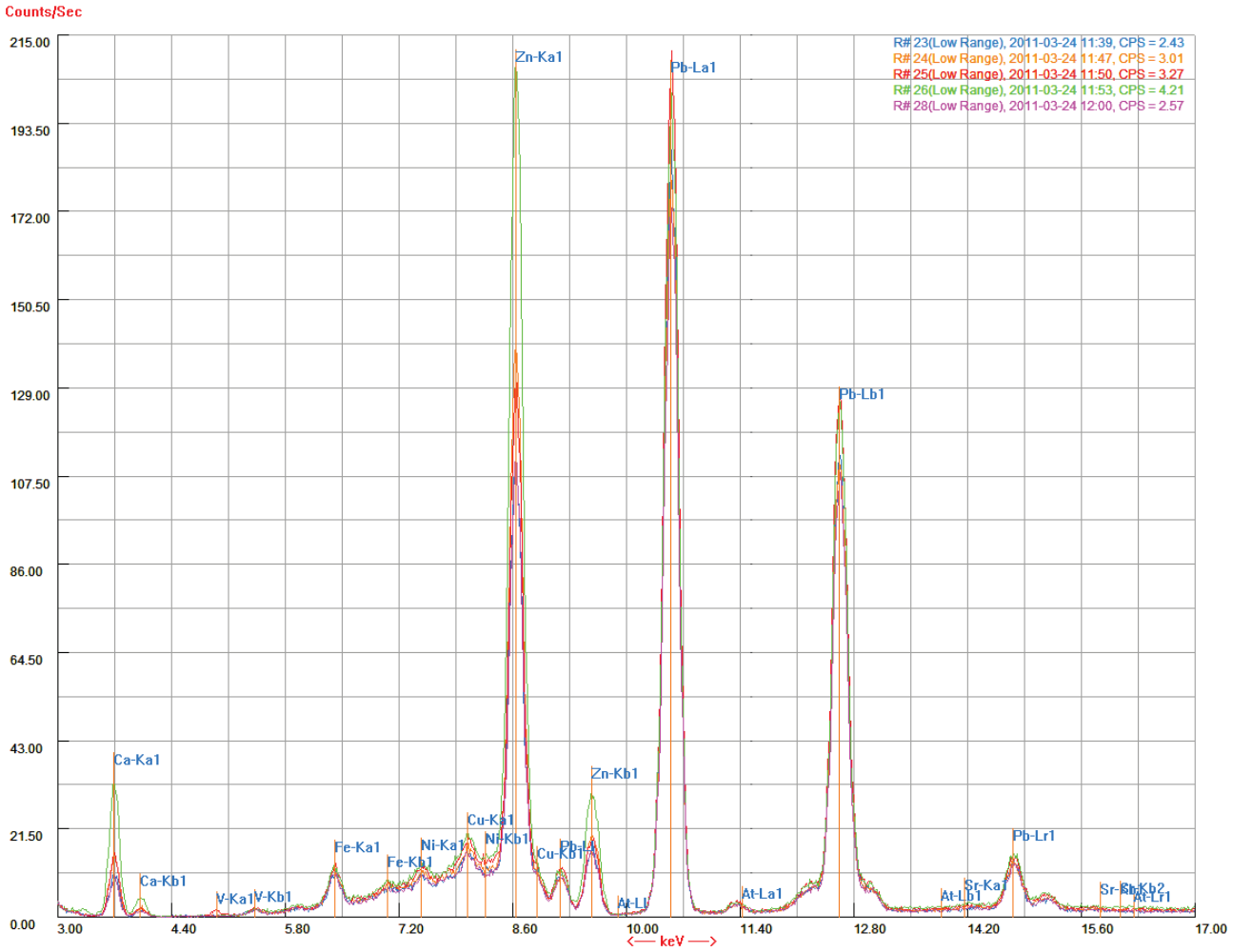

Zn – original?

Sr – XRF highly sensitive – commonly seen associated with Ca (ground) material

Ni, Fe – can be from instrument

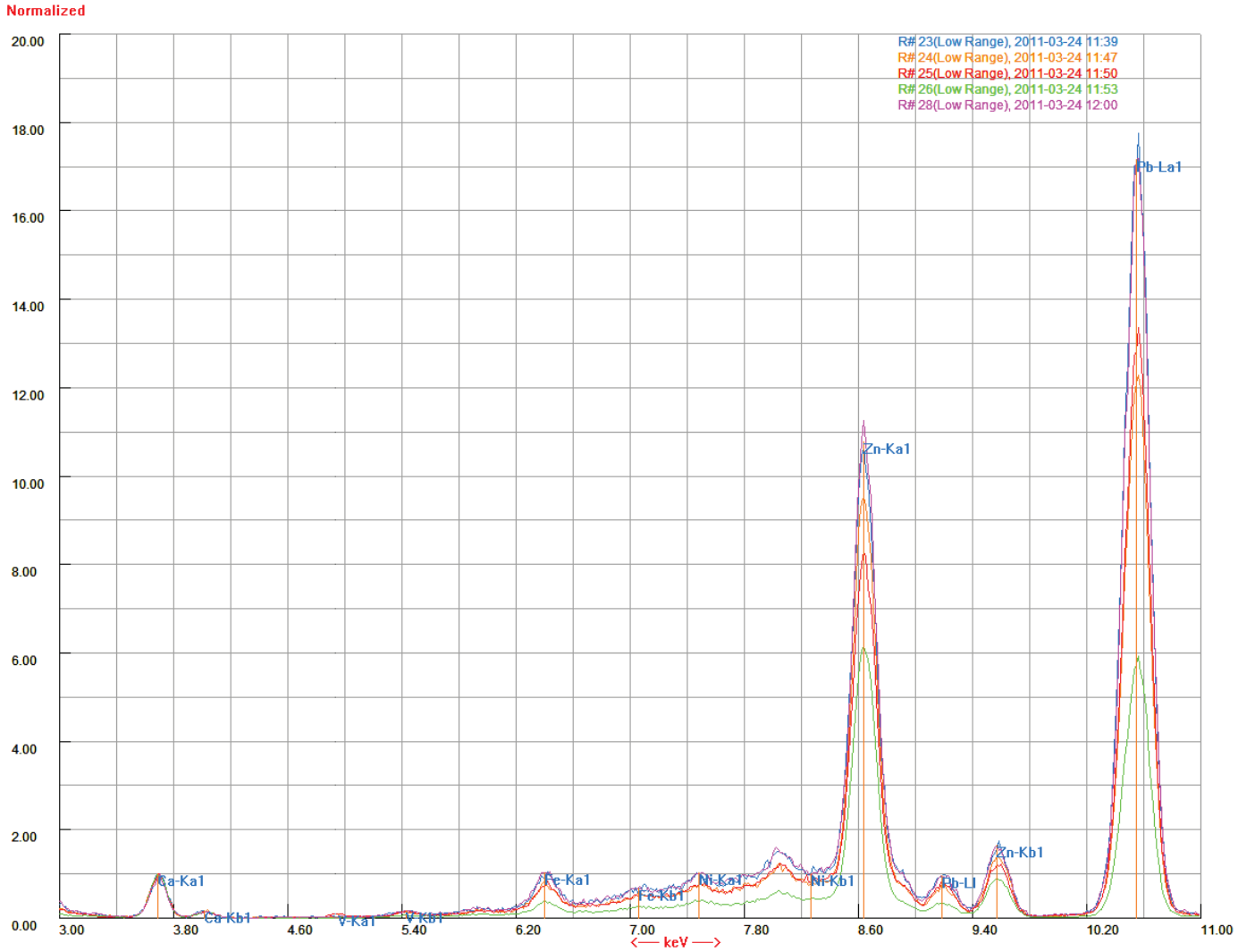
**Low range**

See small vanadium (V) peak in tidemark area but not detected in other spectra across the transect. Also see Cu (in all spectra – probably instrument contribution).

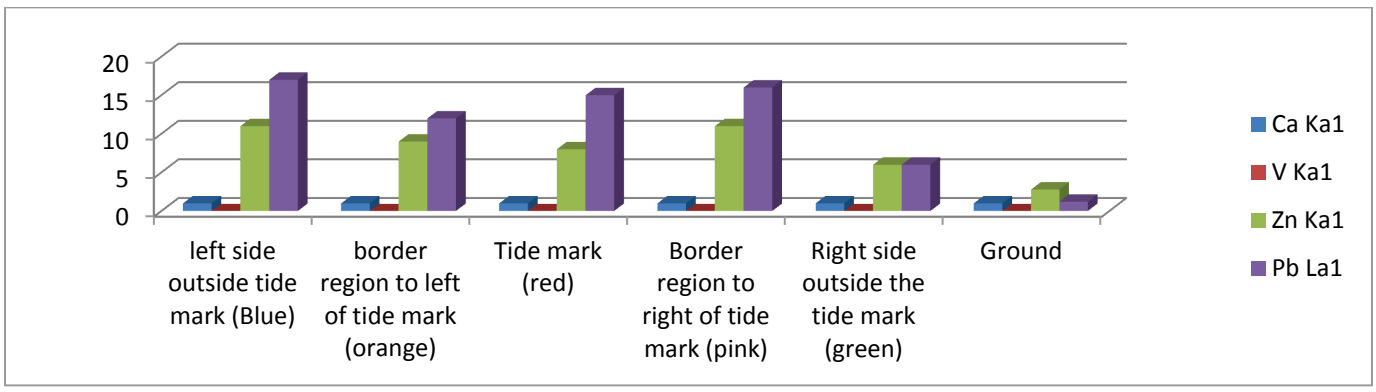


Low range normalised on calcium Ka1 line to show ratio of Ca Ka1 : Zn Ka1 : Pb La1.

Normalisation means that the main calcium peak is equalised in all spectra, and so the other element peaks are increased or decreased proportionally. Hence a ratio with the calcium peak can be obtained that is comparable between all spectra.

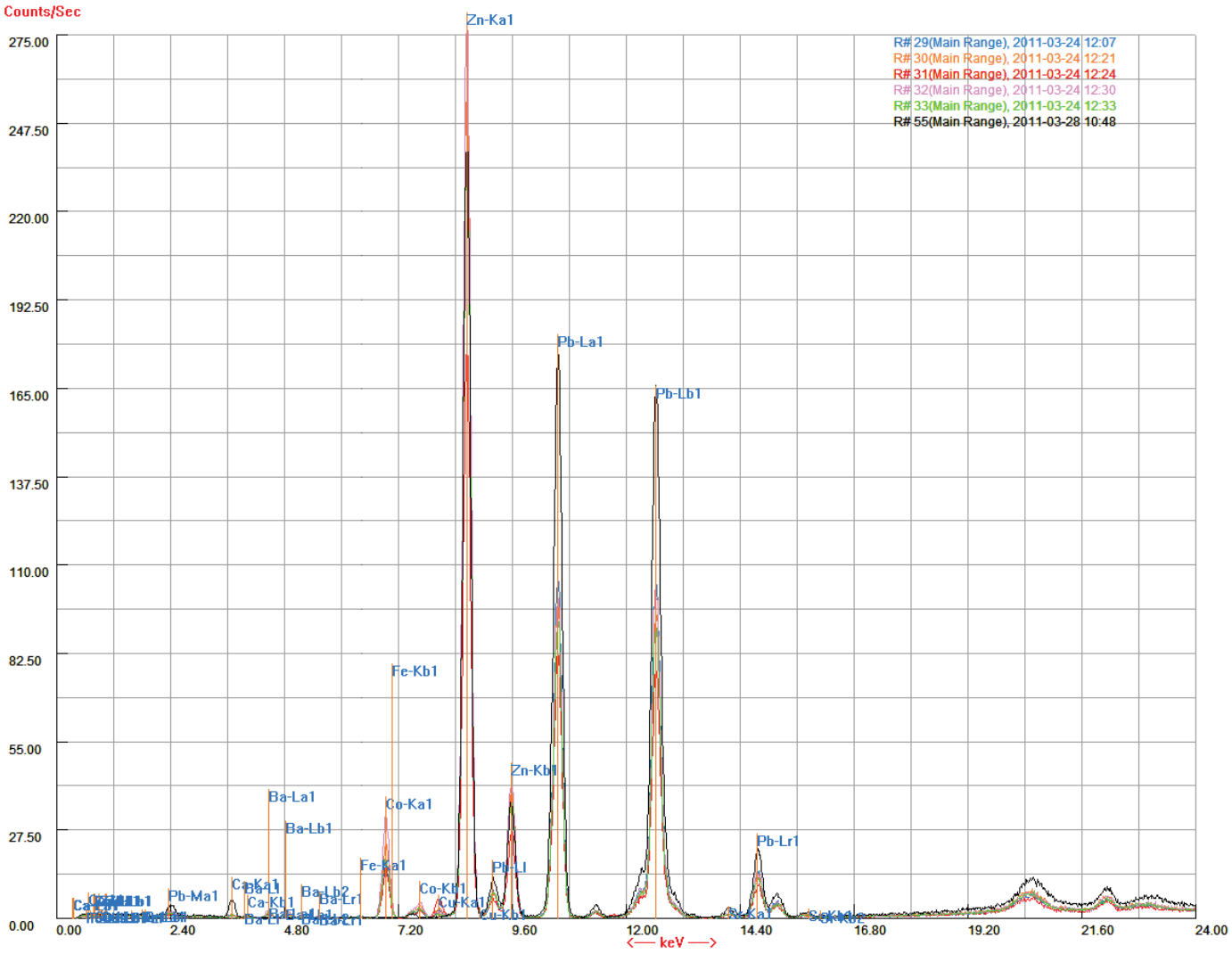



| | Ratio | | | |
|---|---|---|---|---|
| **Location** | **Ca Ka1** | **V Ka1** | **Zn Ka1** | **Pb La1** |
| 1,1 left side outside tide mark (Blue) | 1 | 0 | 11 | 17 |
| 1,2 border region to left of tide mark (orange) | 1 | 0 | 9 | 12 |
| 1,3 Tide mark (red) | 1 | 0,1 | 8 | 15 |
| 1,4 Border region to right of tide mark (pink) | 1 | 0 | 11 | 16 |
| 1,5 Right side outside the tide mark (green) | 1 | 0 | 6 | 6 |
| 7 Ground | 1 | 0 | 2,8 | 1,2 |



Transect 2

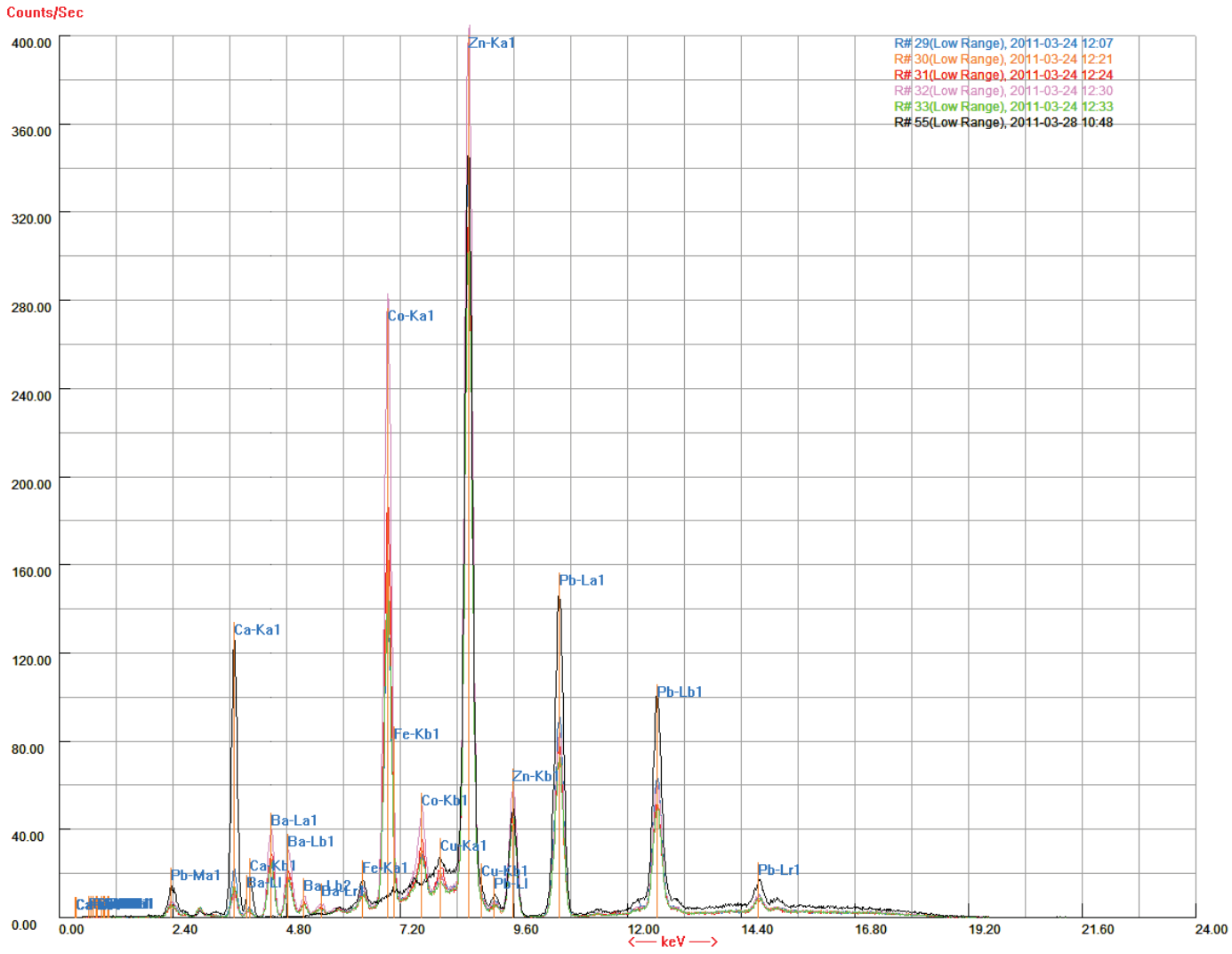
Main range



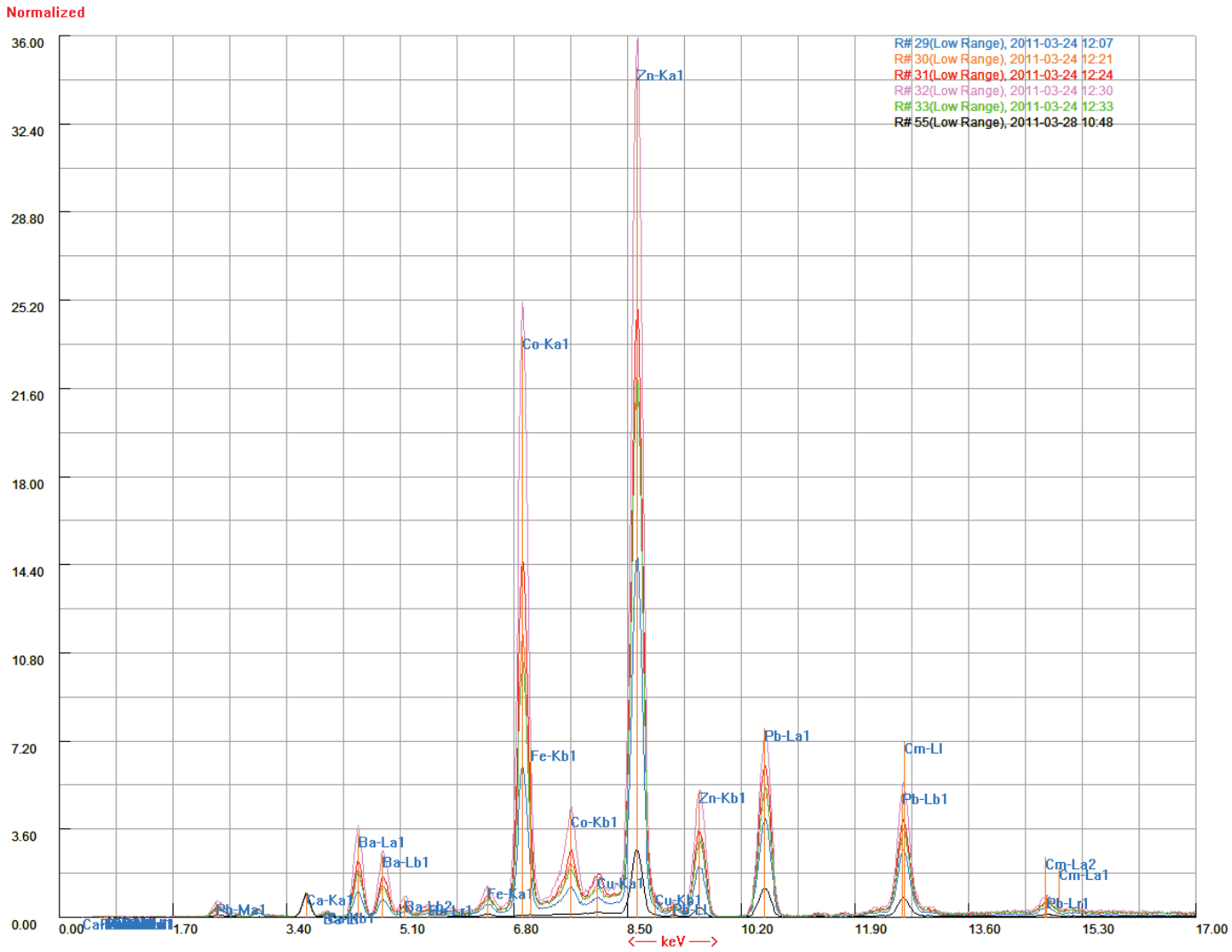

Main peaks: Zn, Pb, Co*, Ca, Ba*, Sr, Cu, Fe

*Not in background spectrum (black)

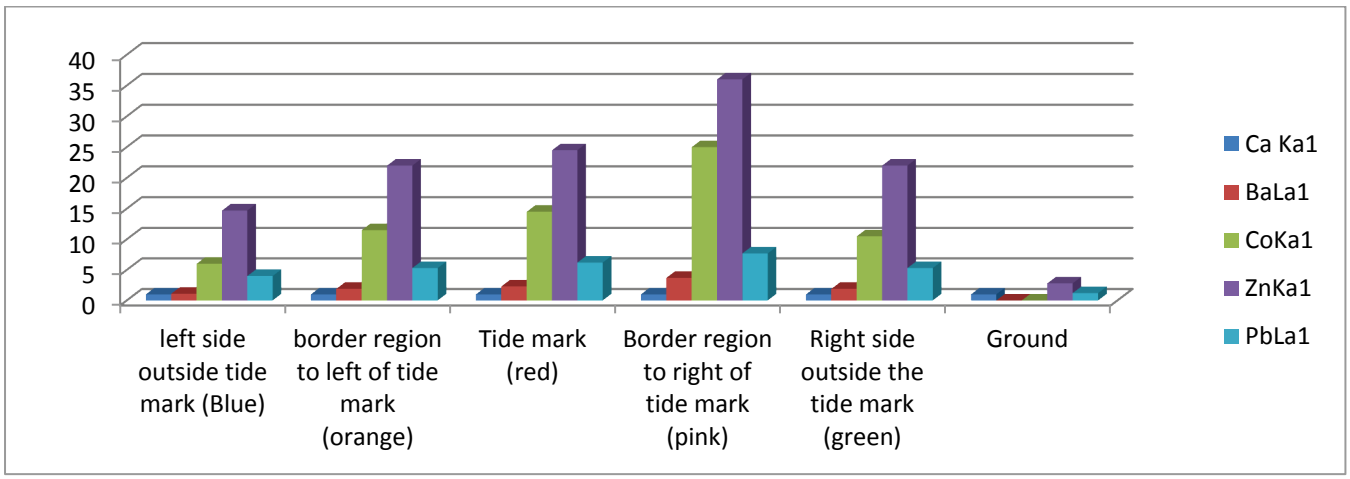
Low range – better view of lighter elements



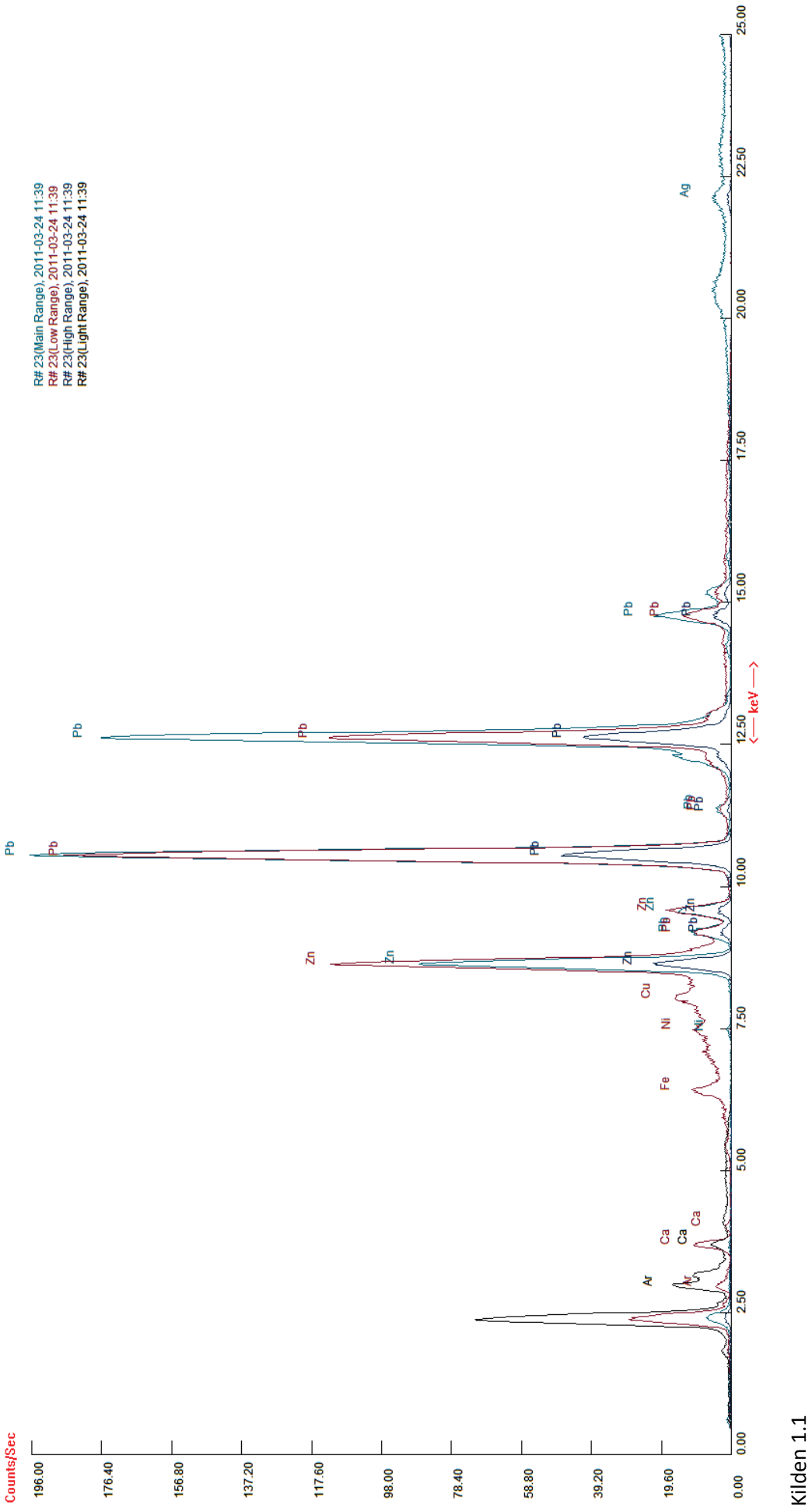
Normalised on Ca Ka1 peak to see ratio with other main elements




| | Ratio | | | | |
|---|---|---|---|---|---|
| **Location** | **Ca Ka1** | **BaLa1** | **CoKa1** | **ZnKa1** | **PbLa1** |
| left side outside tide mark (Blue) | 1 | 1,1 | 6 | 14,7 | 4 |
| border region to left of tide mark (orange) | 1 | 1,9 | 11,5 | 22 | 5,3 |
| Tide mark (red) | 1 | 2,3 | 14,5 | 24,5 | 6,2 |
| Border region to right of tide mark (pink) | 1 | 3,7 | 25 | 36 | 7,7 |
| Right side outside the tide mark (green) | 1 | 1,9 | 10,5 | 22 | 5,3 |
| Ground | 1 | 0 | 0 | 2,8 | 1,2 |

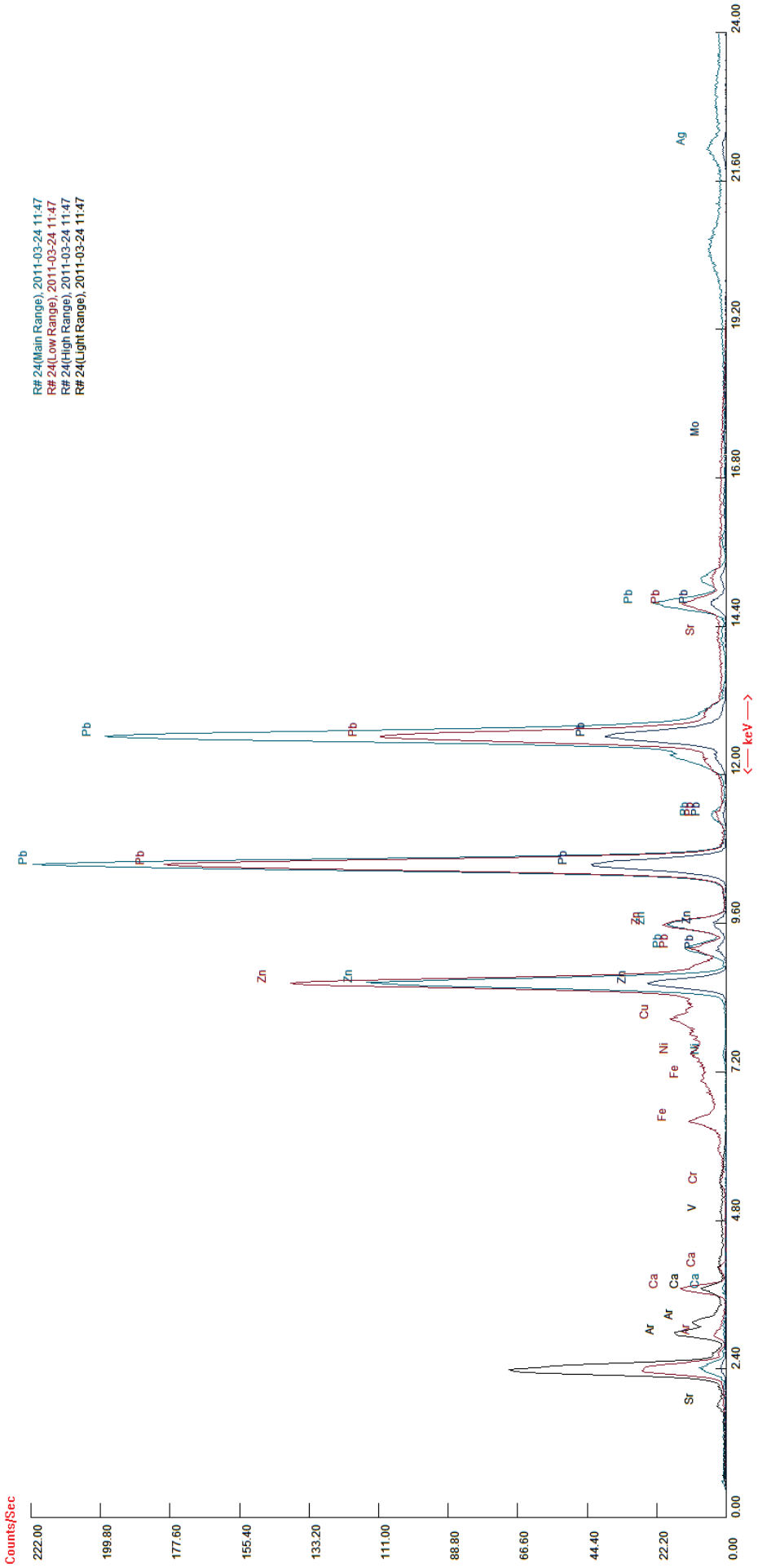


# APPENDIX 3: XRF SPECTRAS



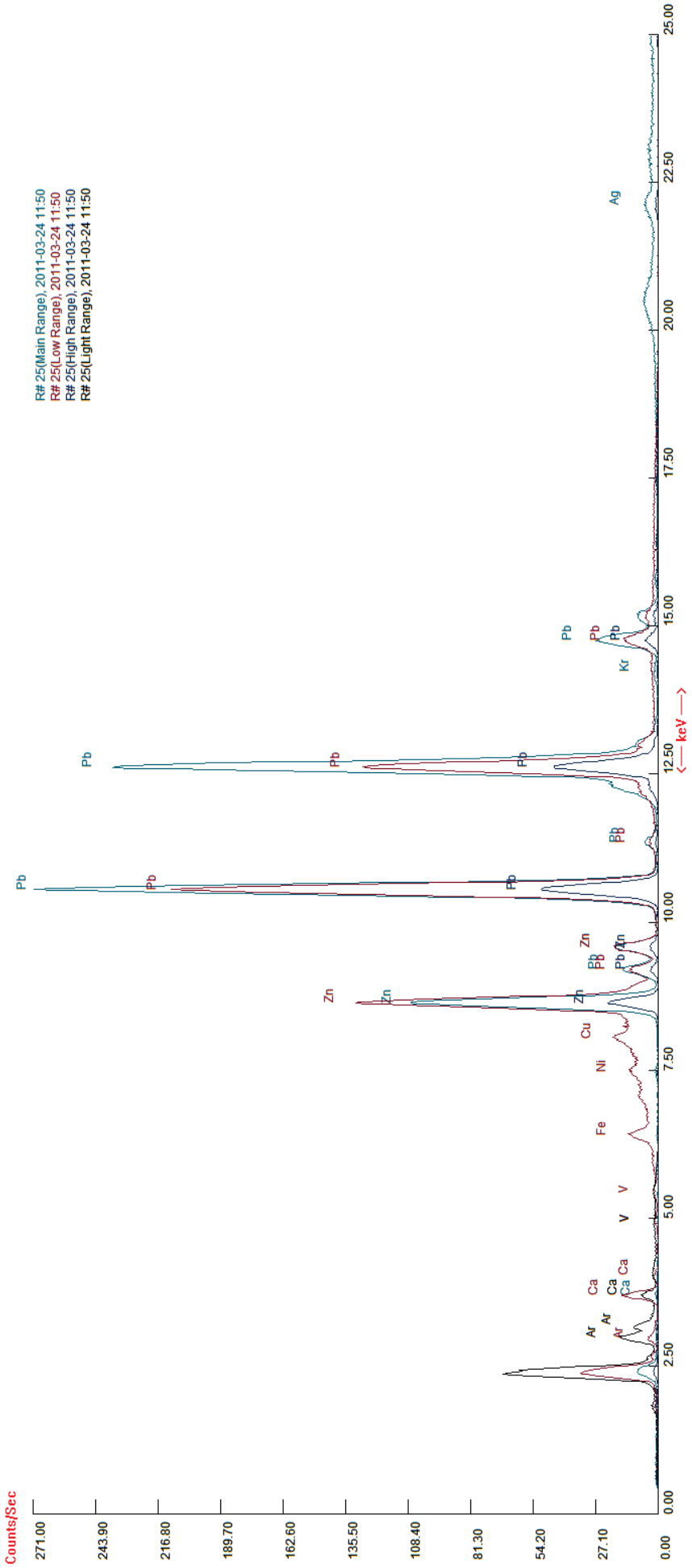

Kilden 1.1

# APPENDIX 3: XRF SPECTRAS



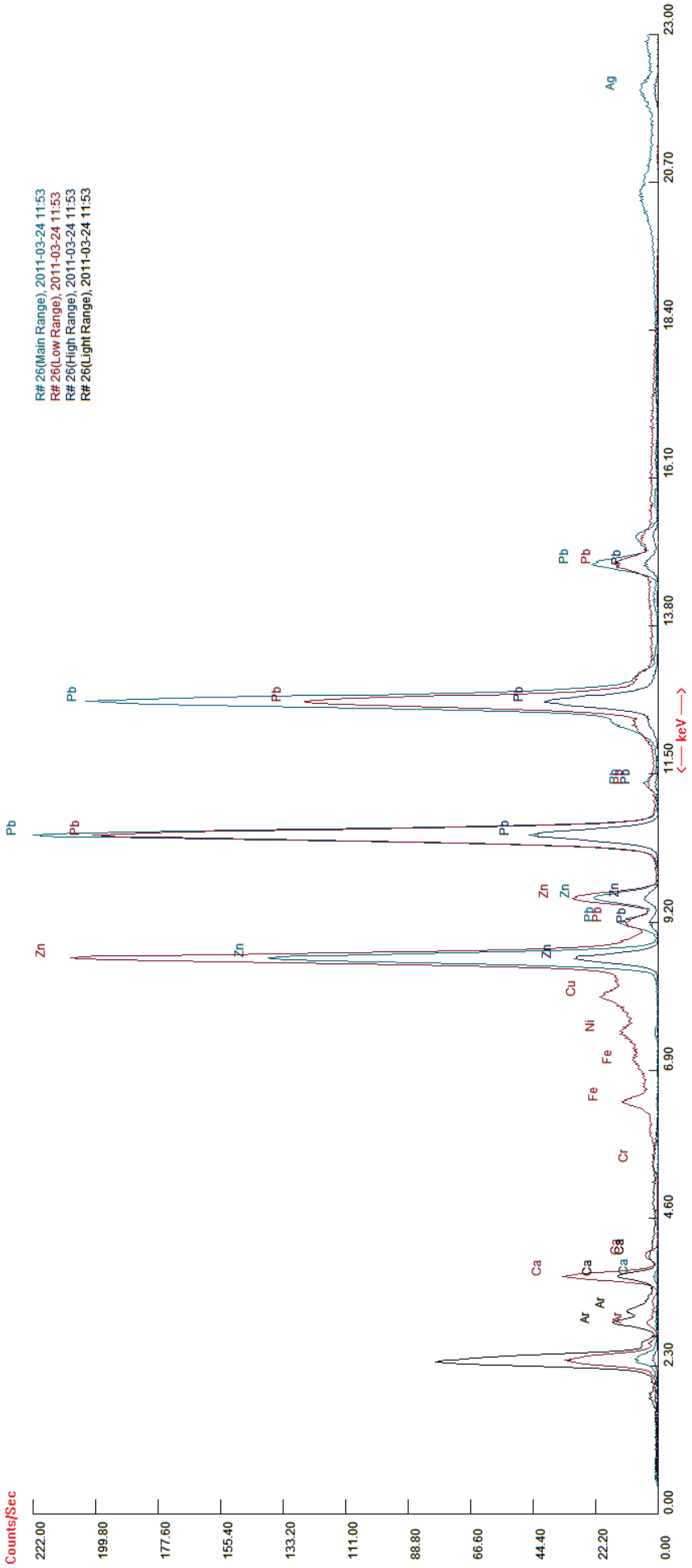

Kilden 1.2

# APPENDIX 3: XRF SPECTRAS



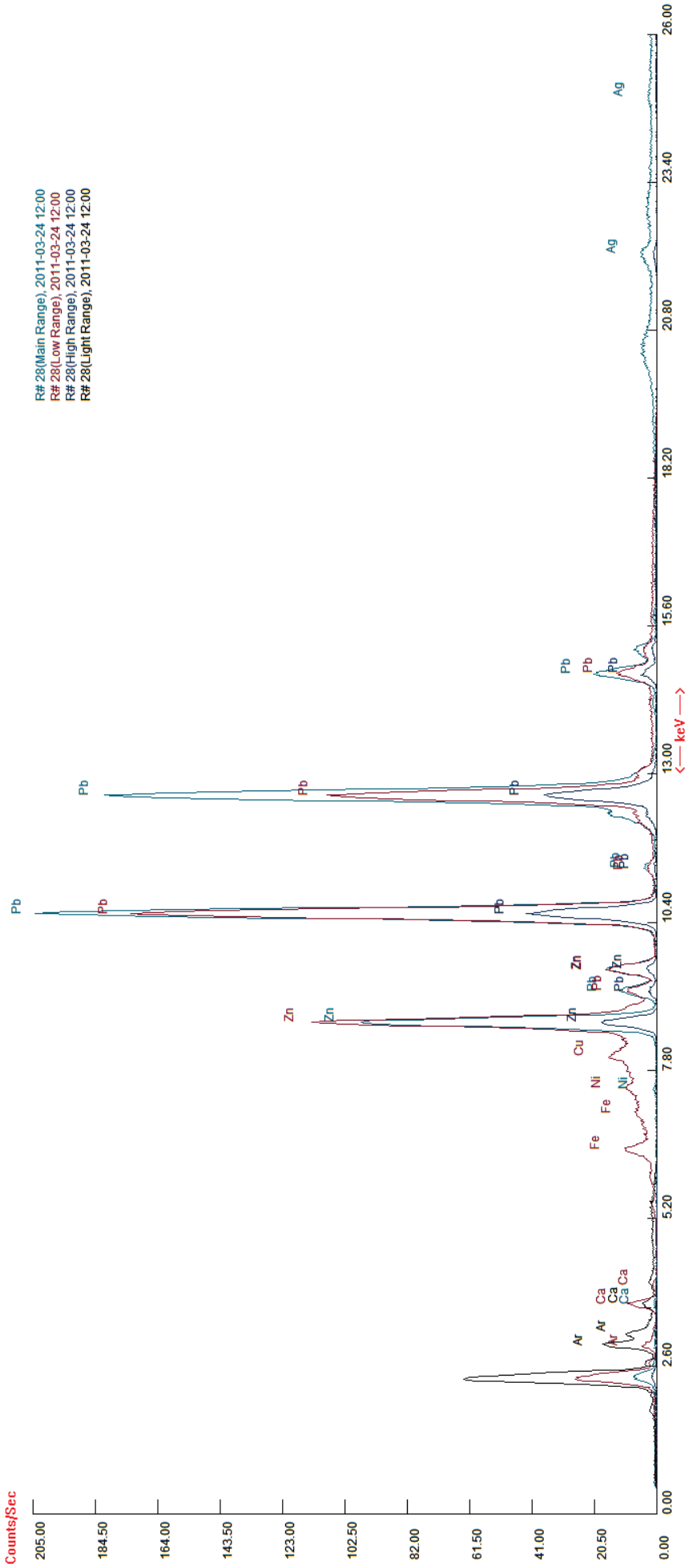

Kilden 1.3

# APPENDIX 3: XRF SPECTRAS



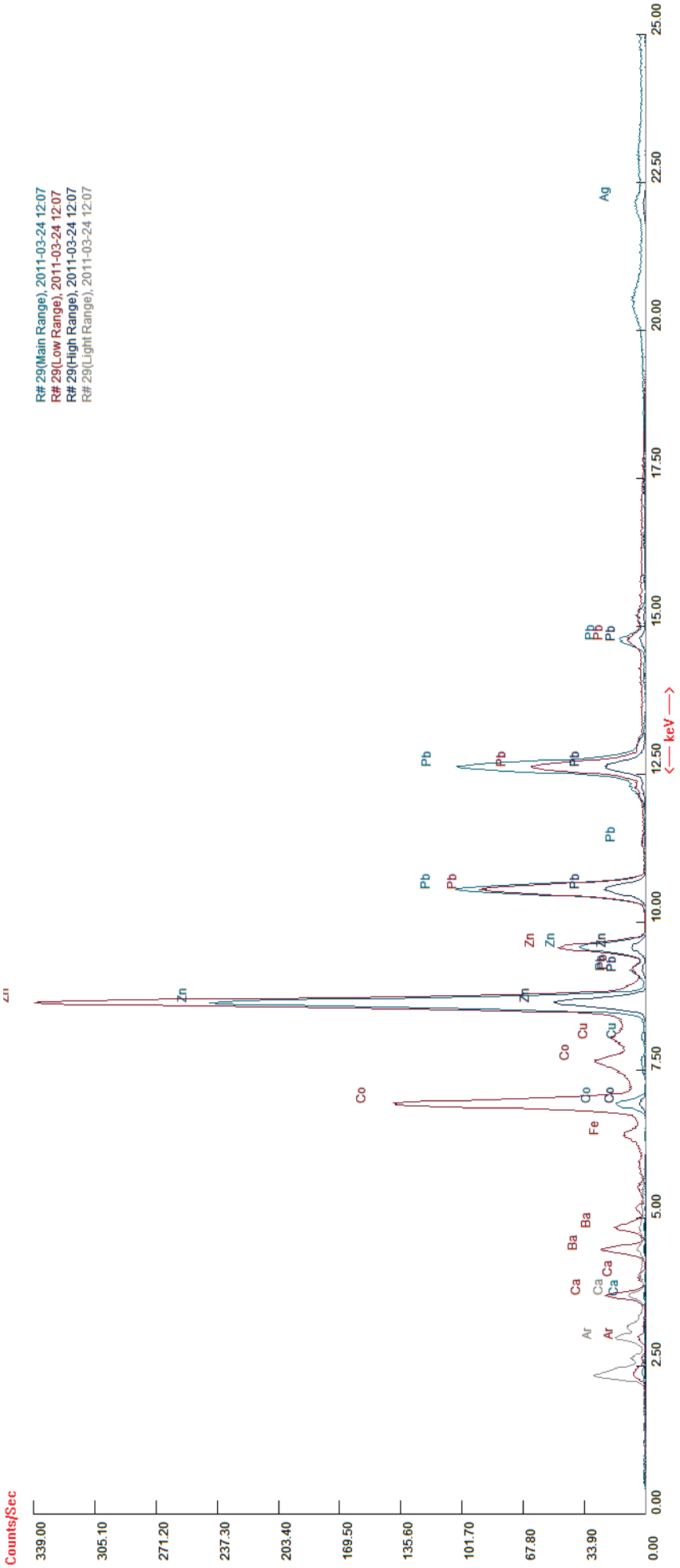

Kilden 1.4

# APPENDIX 3: XRF SPECTRAS



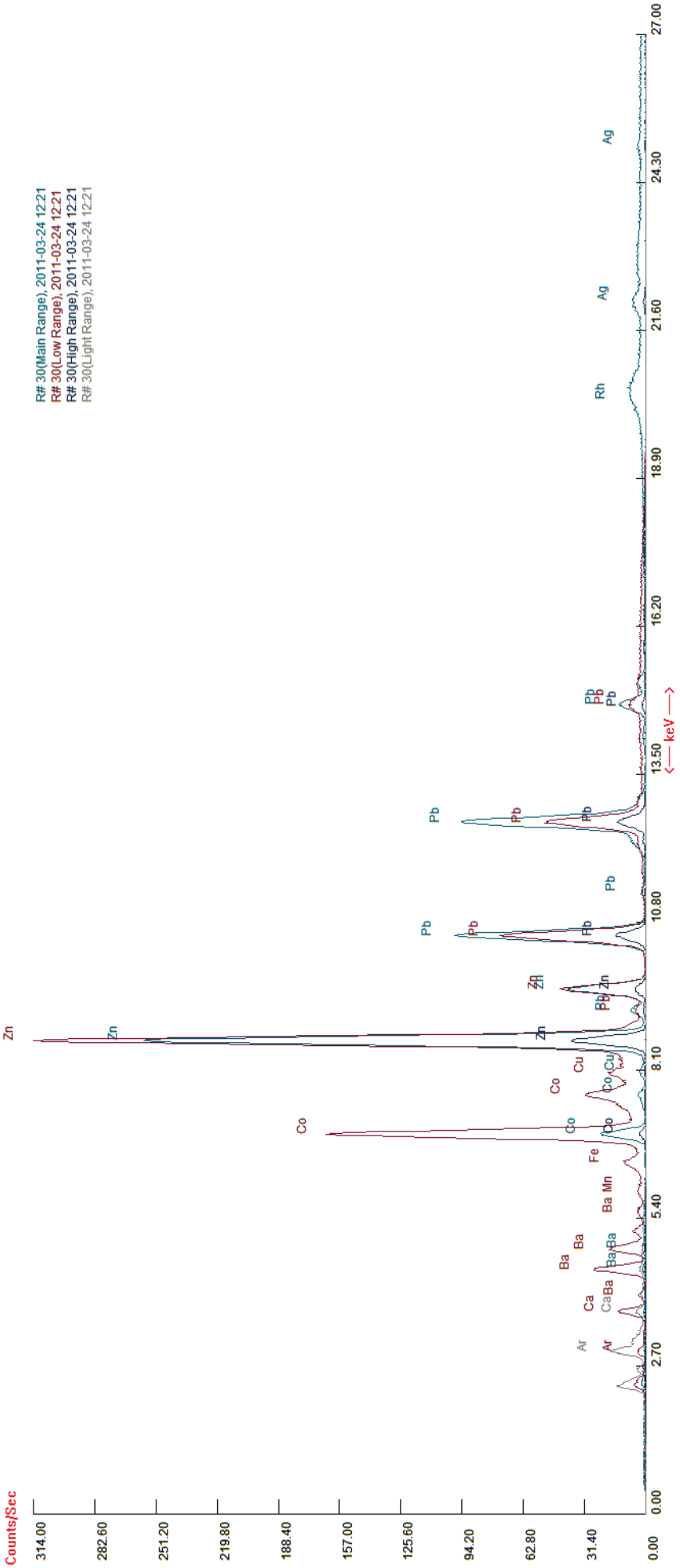

Kilden 1.5

# APPENDIX 3: XRF SPECTRAS



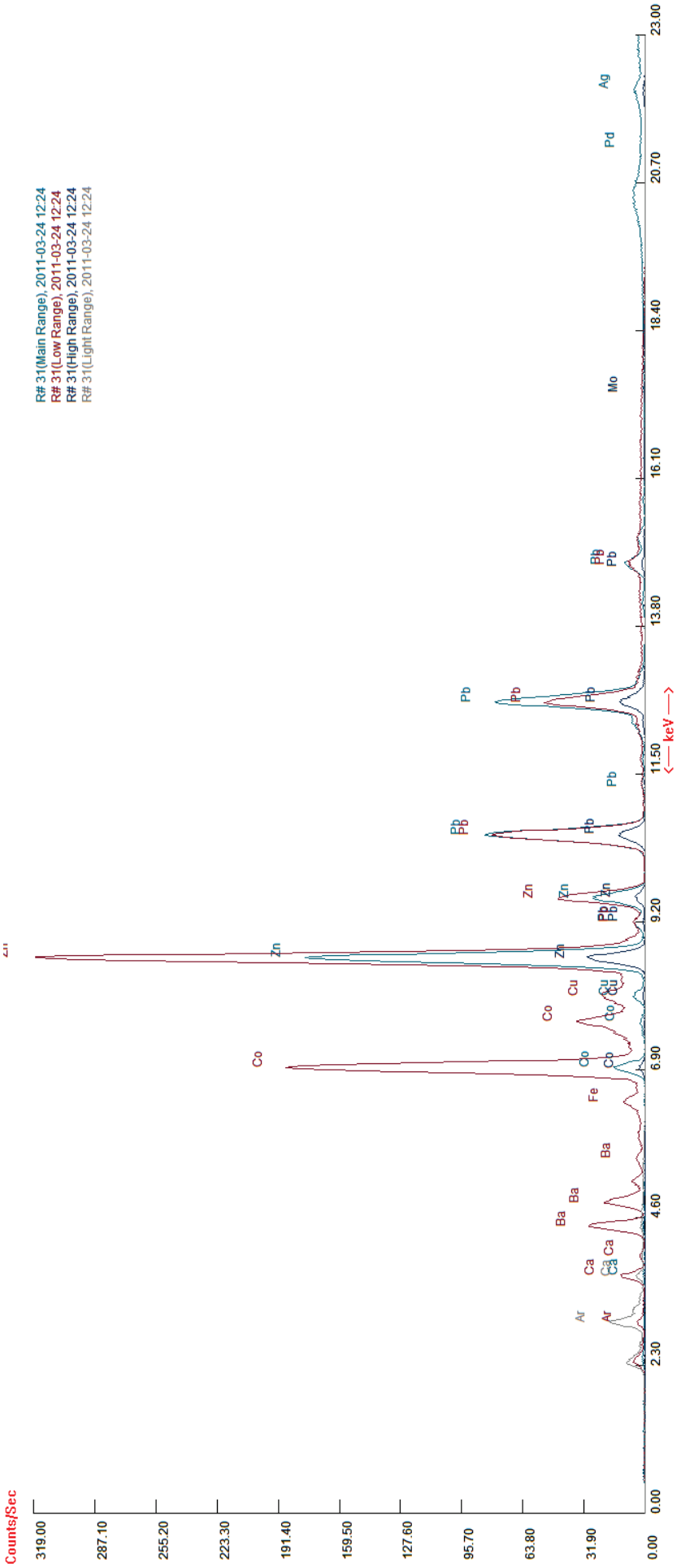

Kilden 2.1

# APPENDIX 3: XRF SPECTRAS



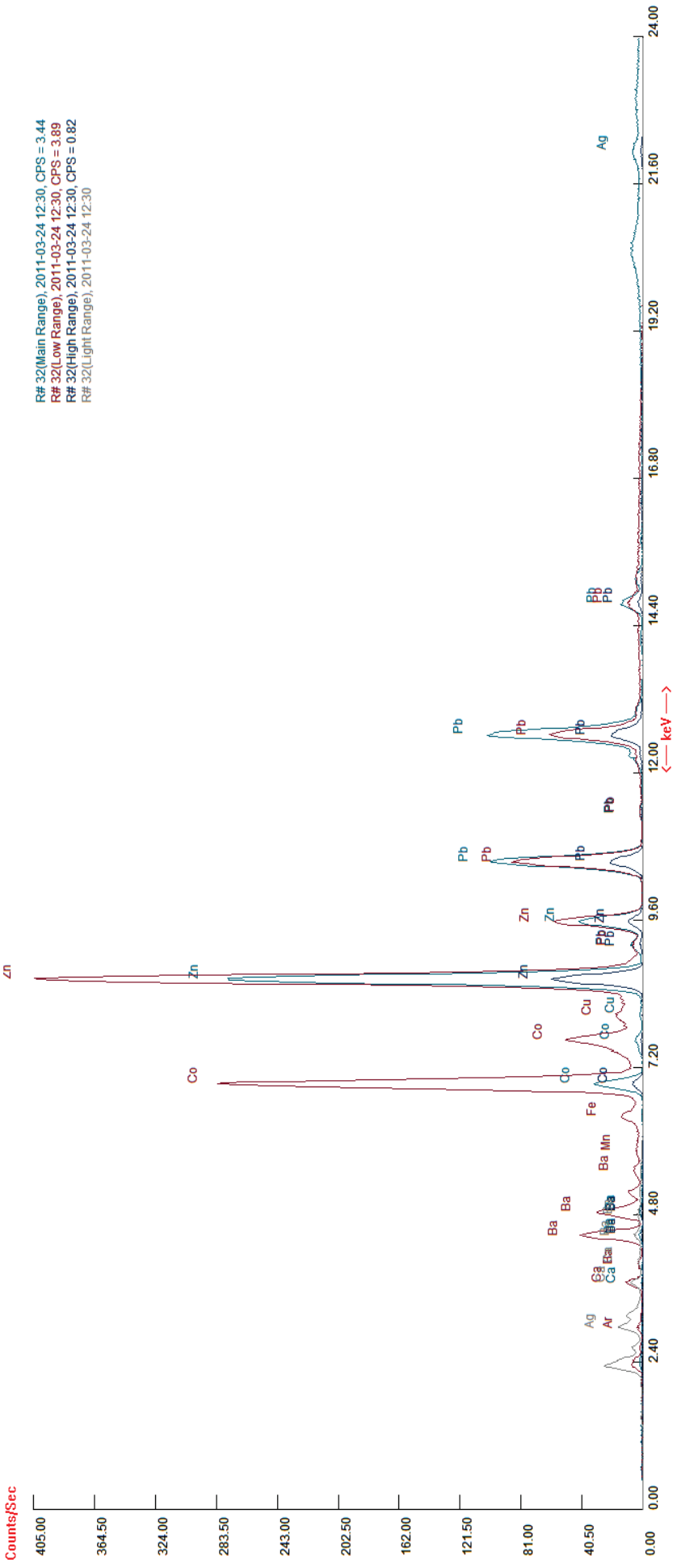

Kilden 2.2

# APPENDIX 3: XRF SPECTRAS



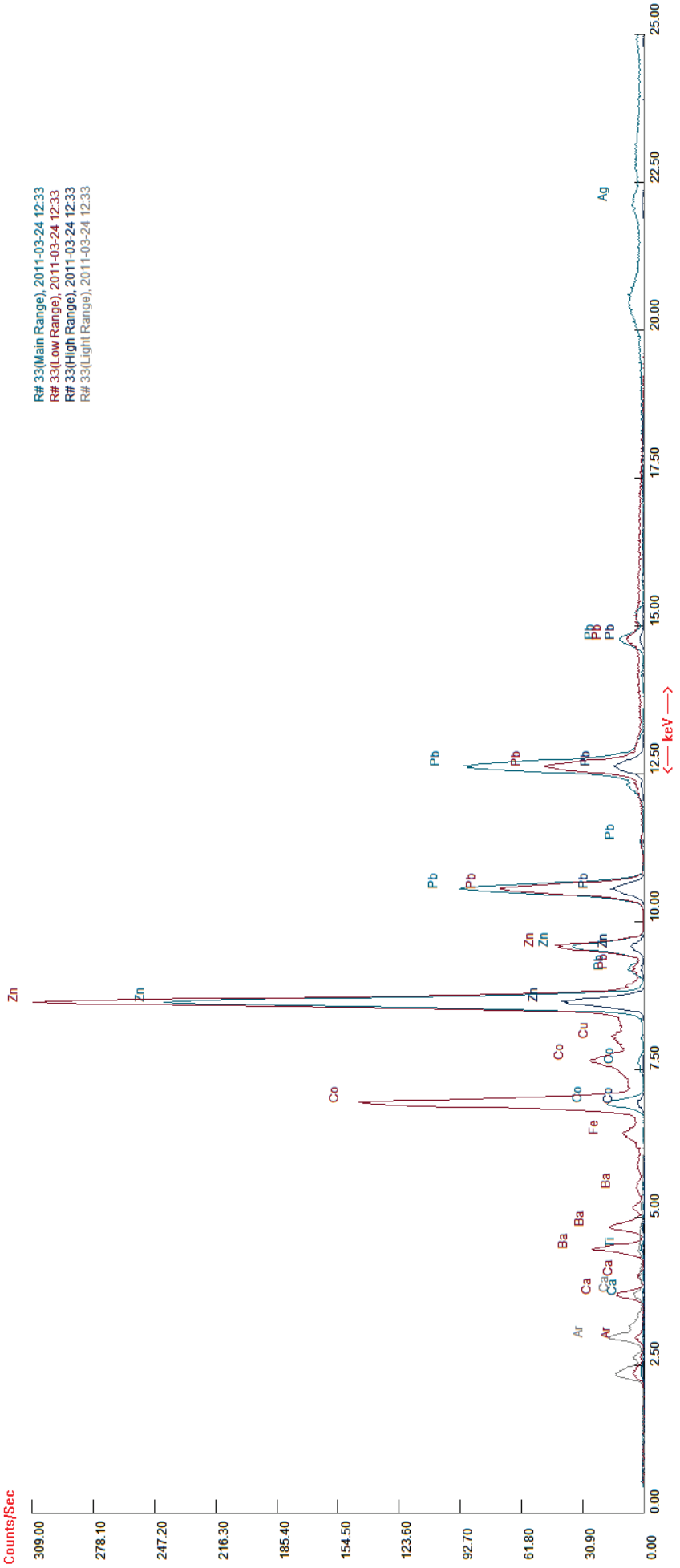

Kilden 2.3

# APPENDIX 3: XRF SPECTRAS



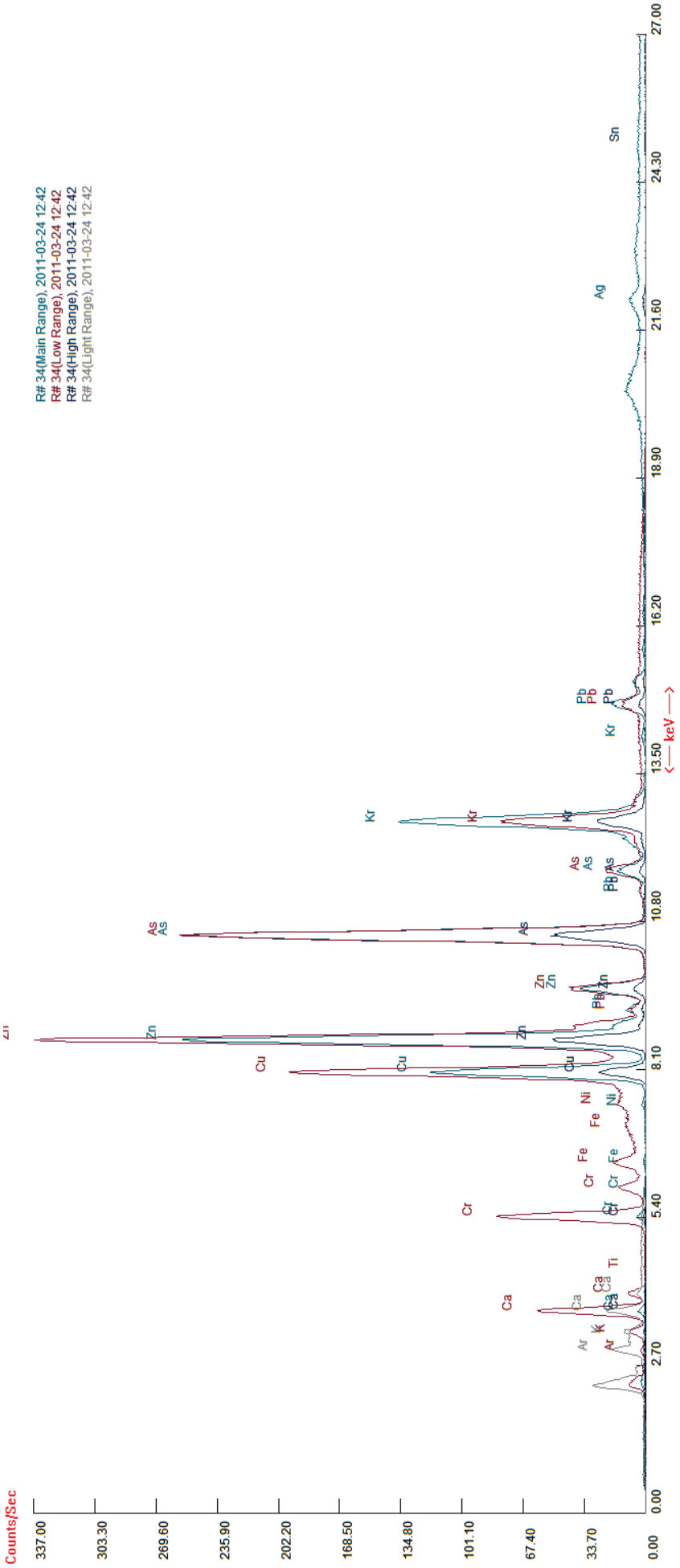

Kilden 2.4

# APPENDIX 3: XRF SPECTRAS



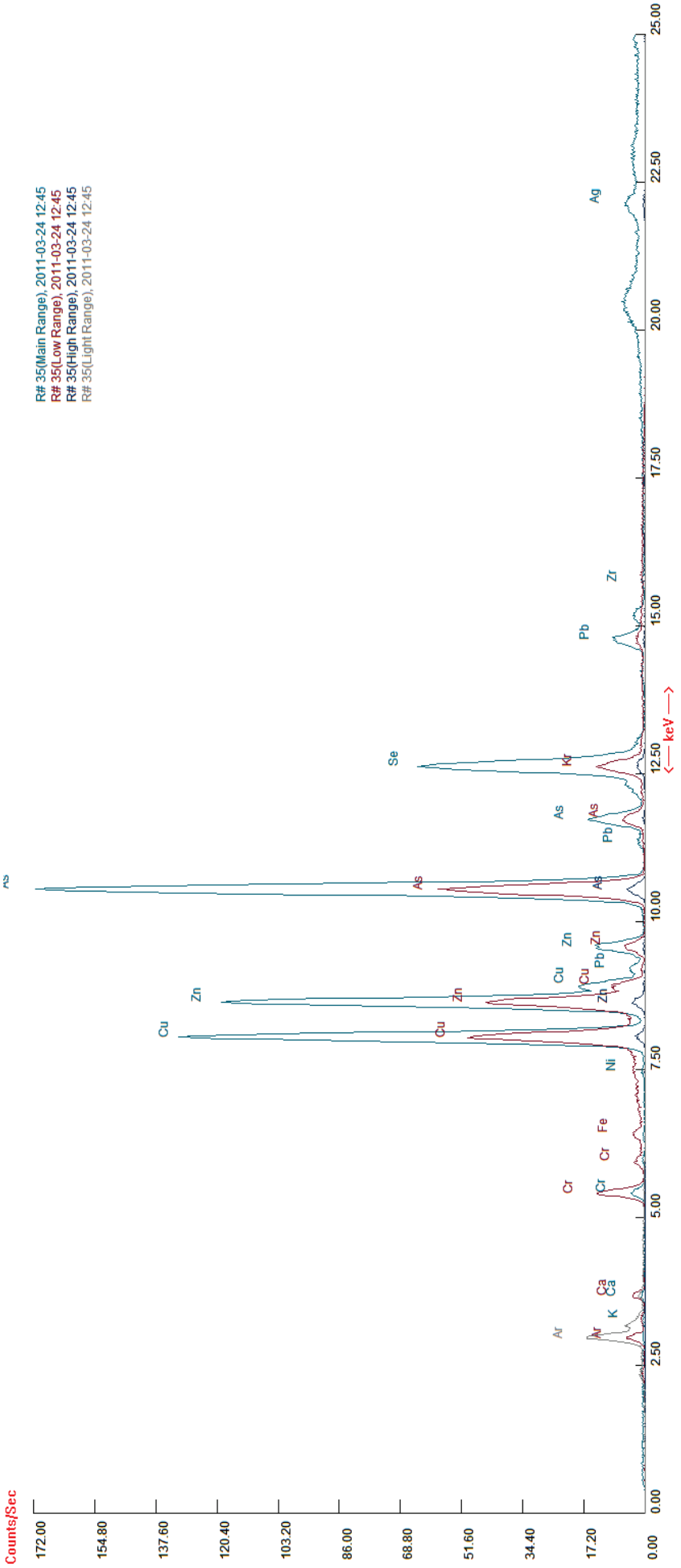

Kilden 2.5

# APPENDIX 3: XRF SPECTRAS



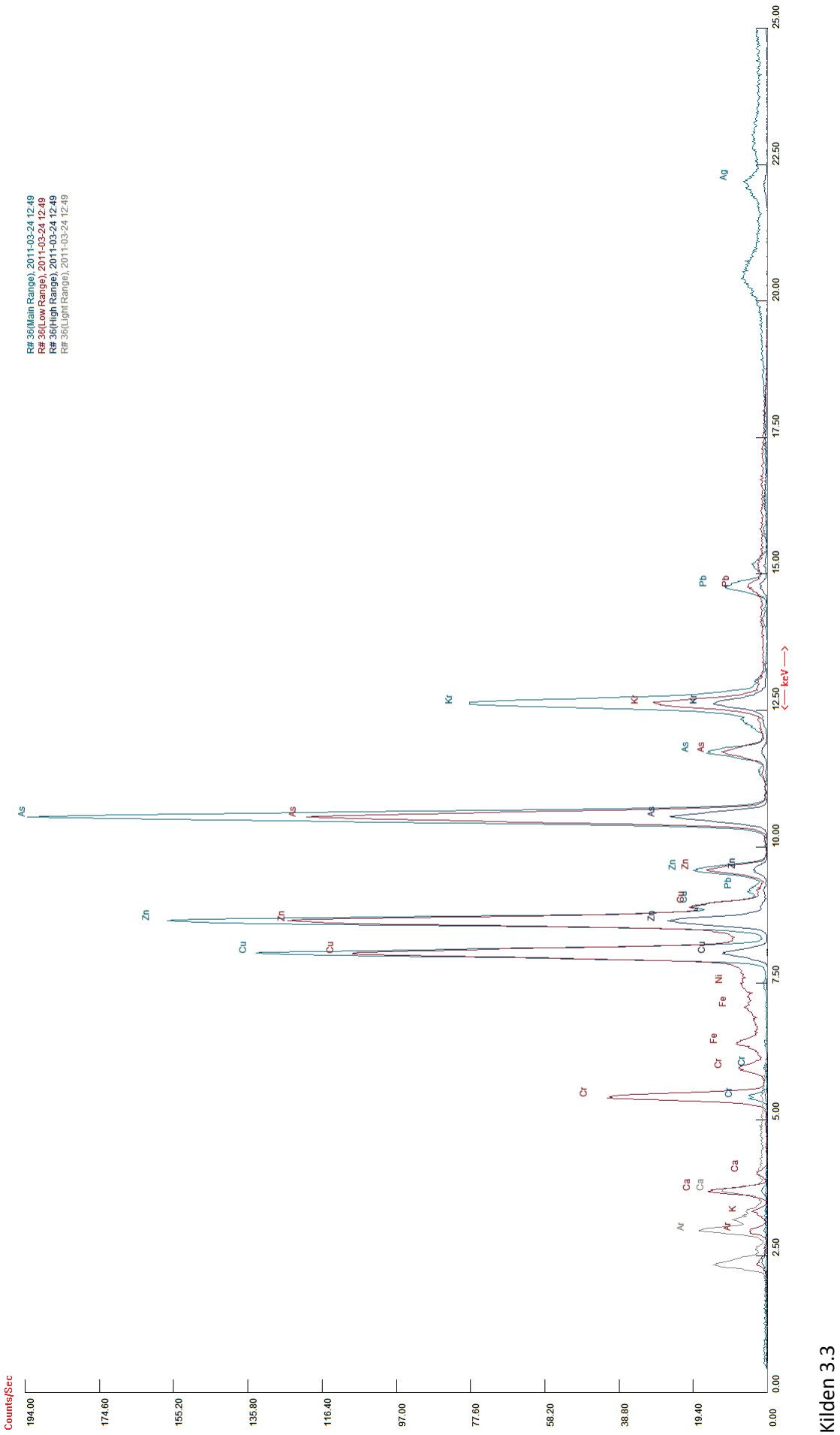

Kilden 3.1

# APPENDIX 3: XRF SPECTRAS



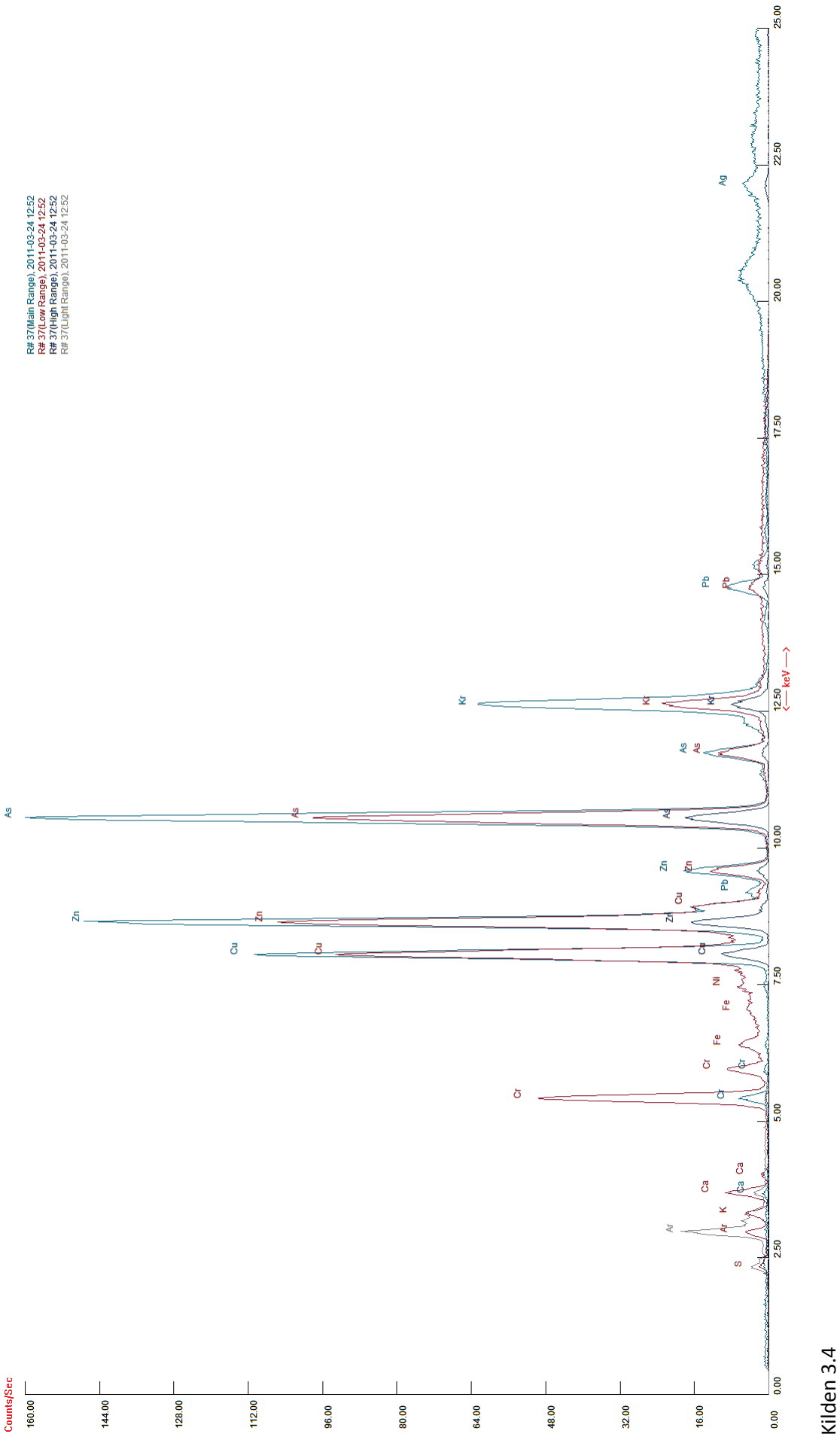

Kilden 3.2

# APPENDIX 3: XRF SPECTRAS

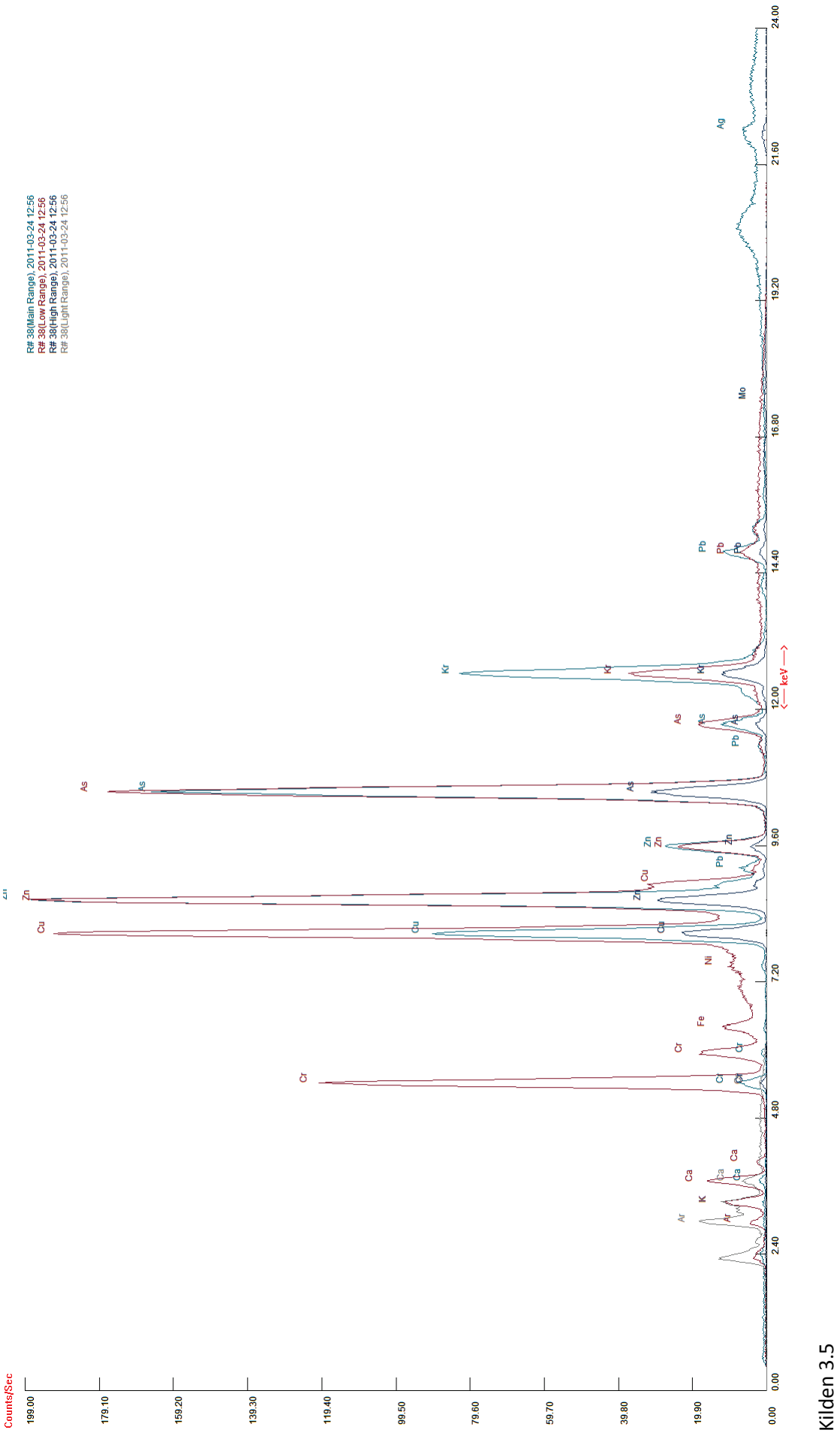



Kilden 3.3

# APPENDIX 3: XRF SPECTRAS

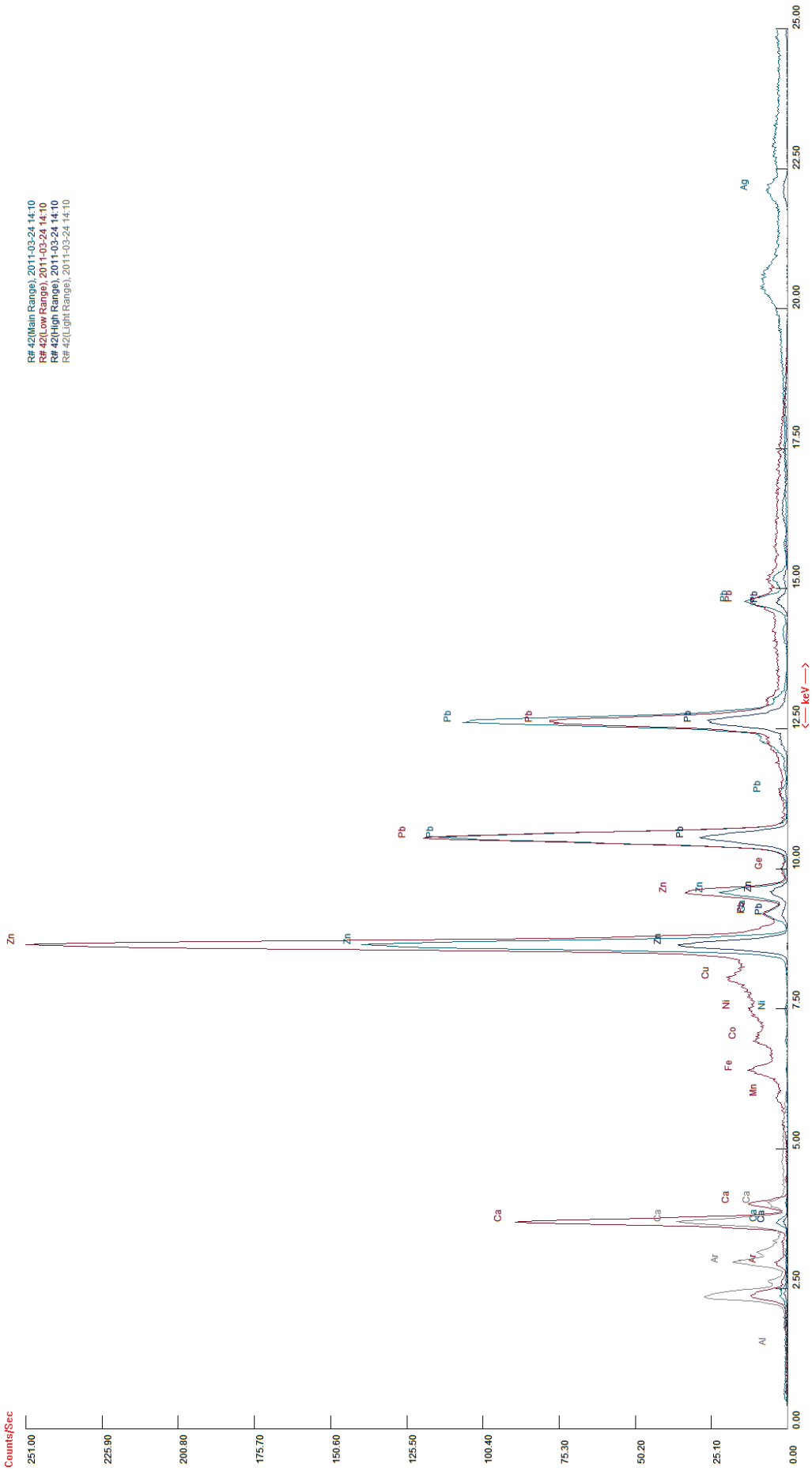


# APPENDIX 3: XRF SPECTRAS



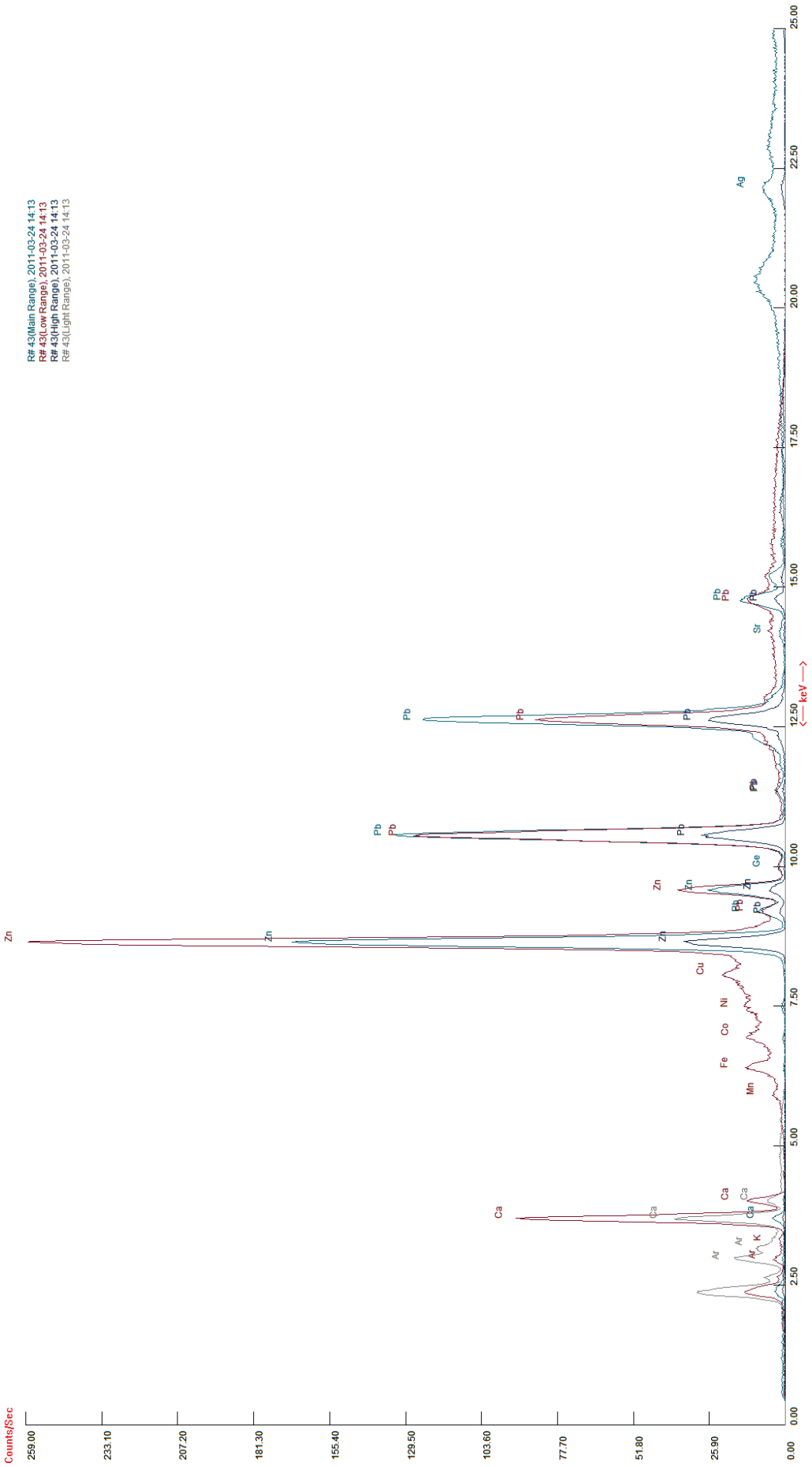

Kilden 3.5

# APPENDIX 3: XRF SPECTRAS



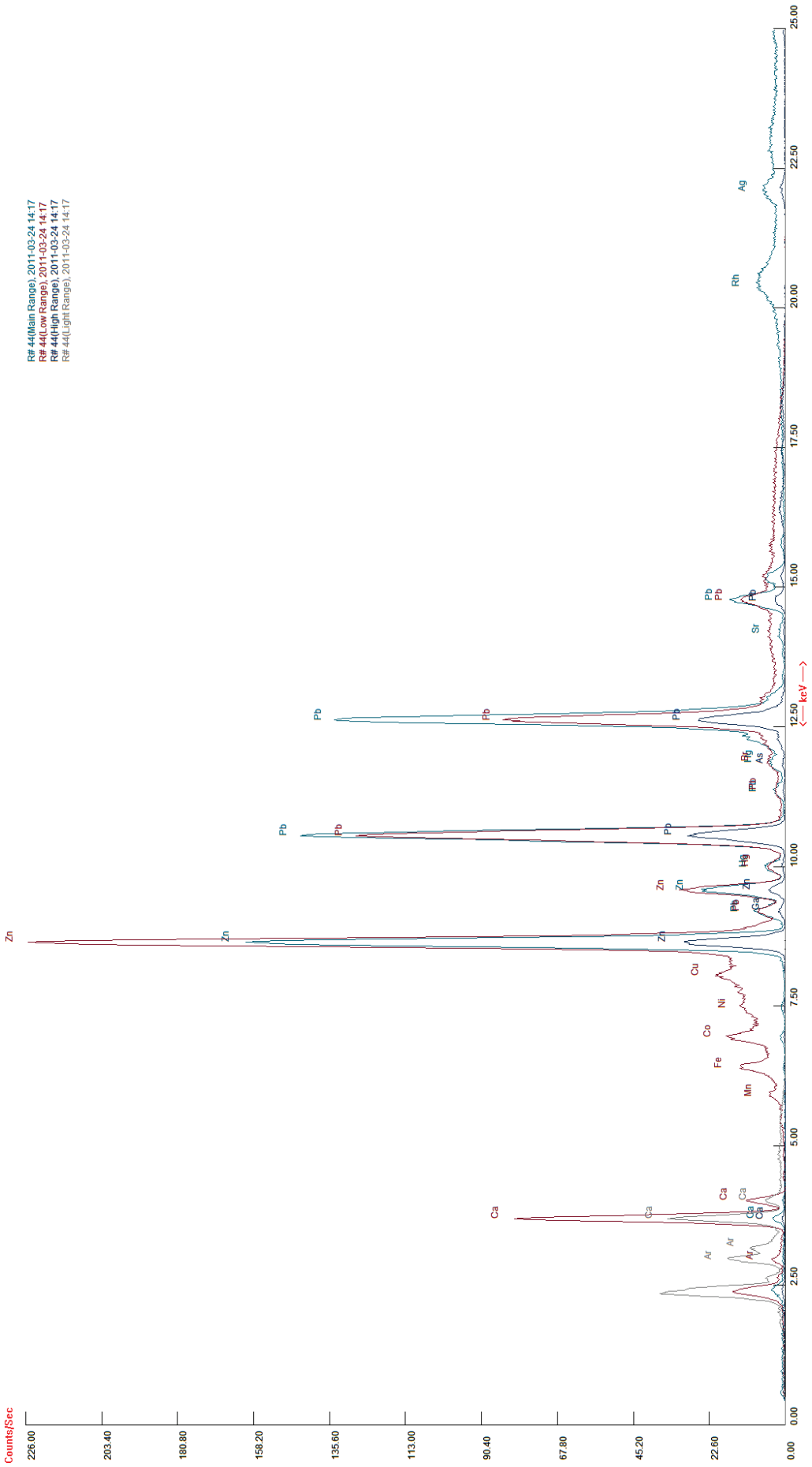

Kilden 4b.1

# APPENDIX 3: XRF SPECTRAS



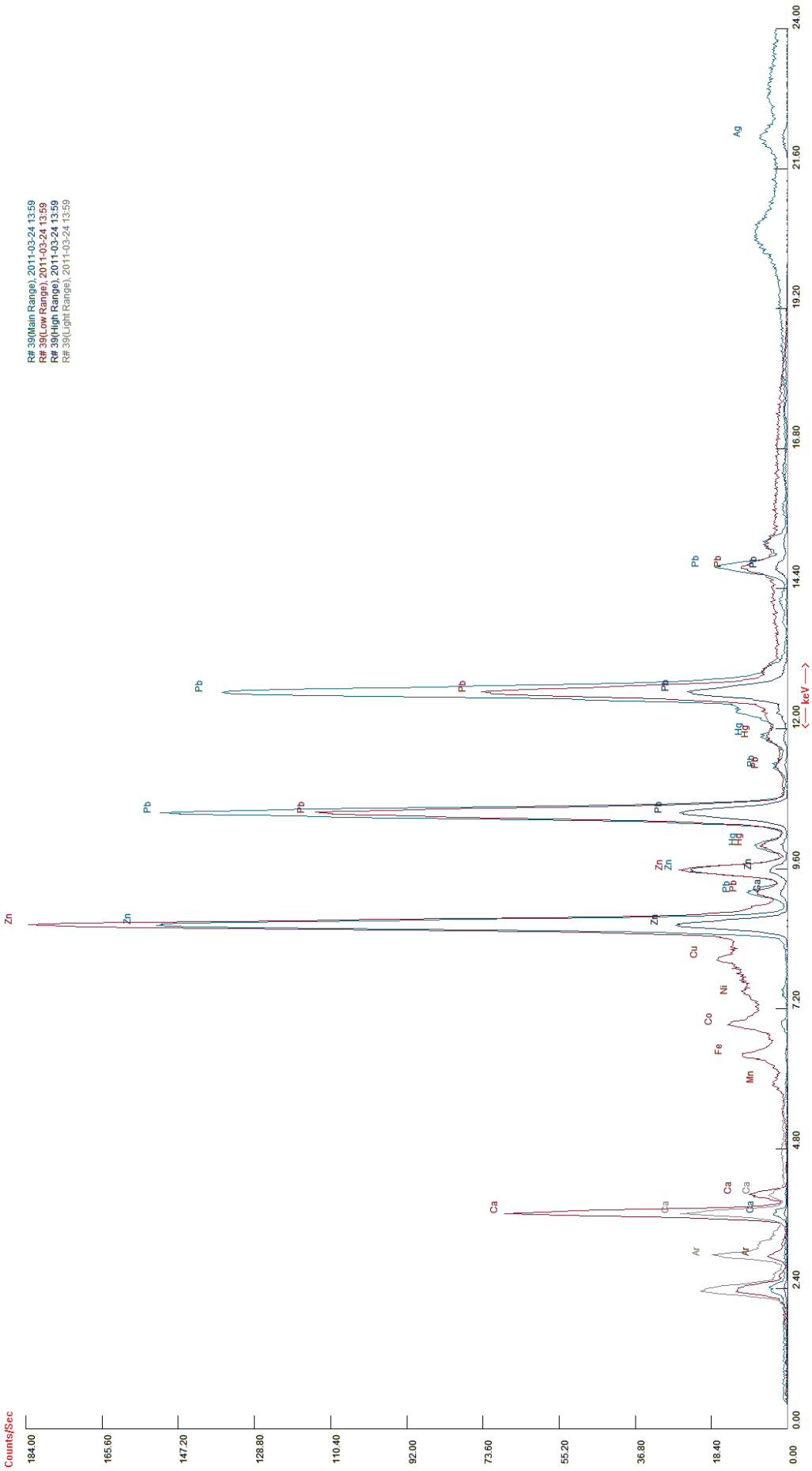

Kilden 4b.2

# APPENDIX 3: XRF SPECTRAS



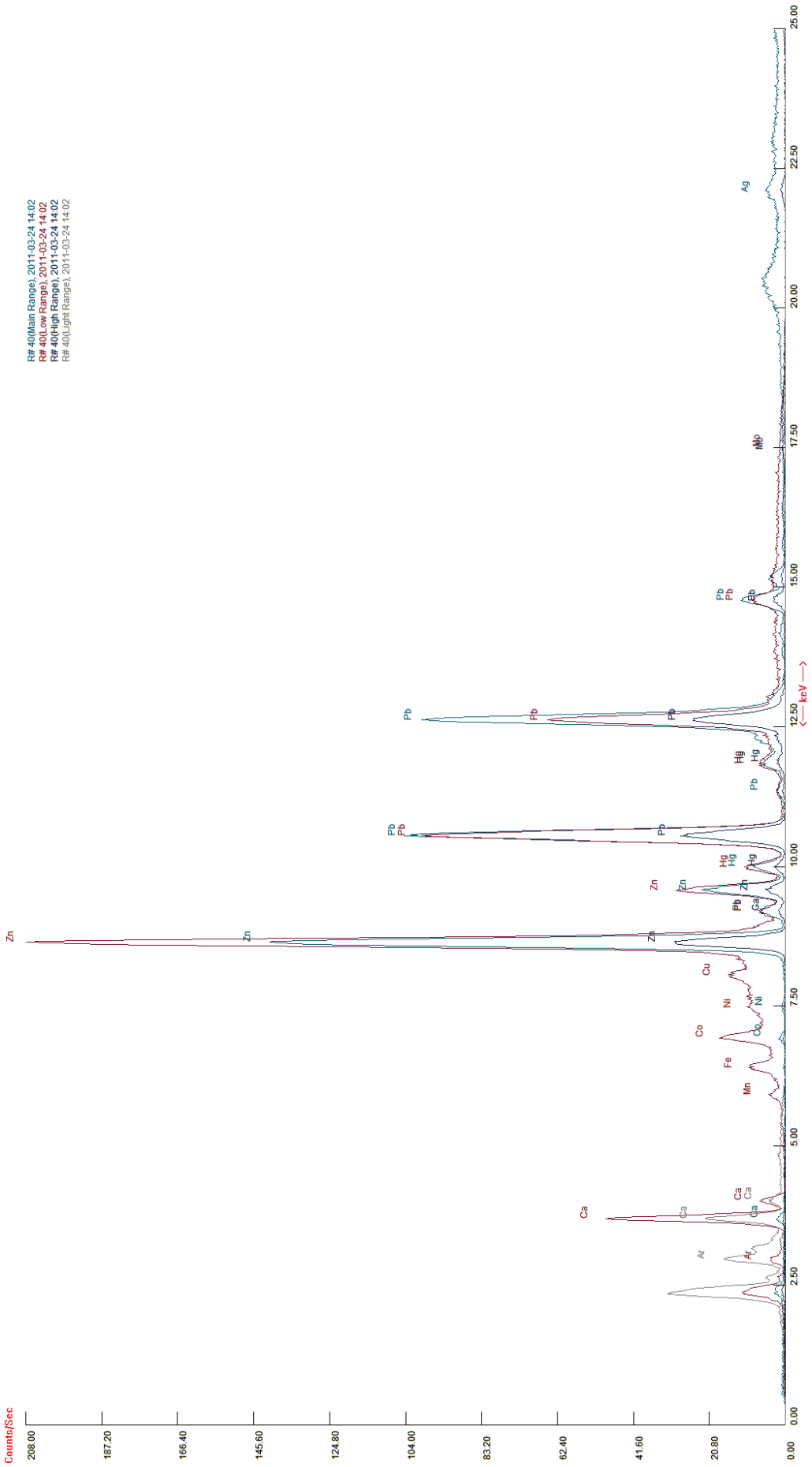

Kilden 4b.3

# APPENDIX 3: XRF SPECTRAS



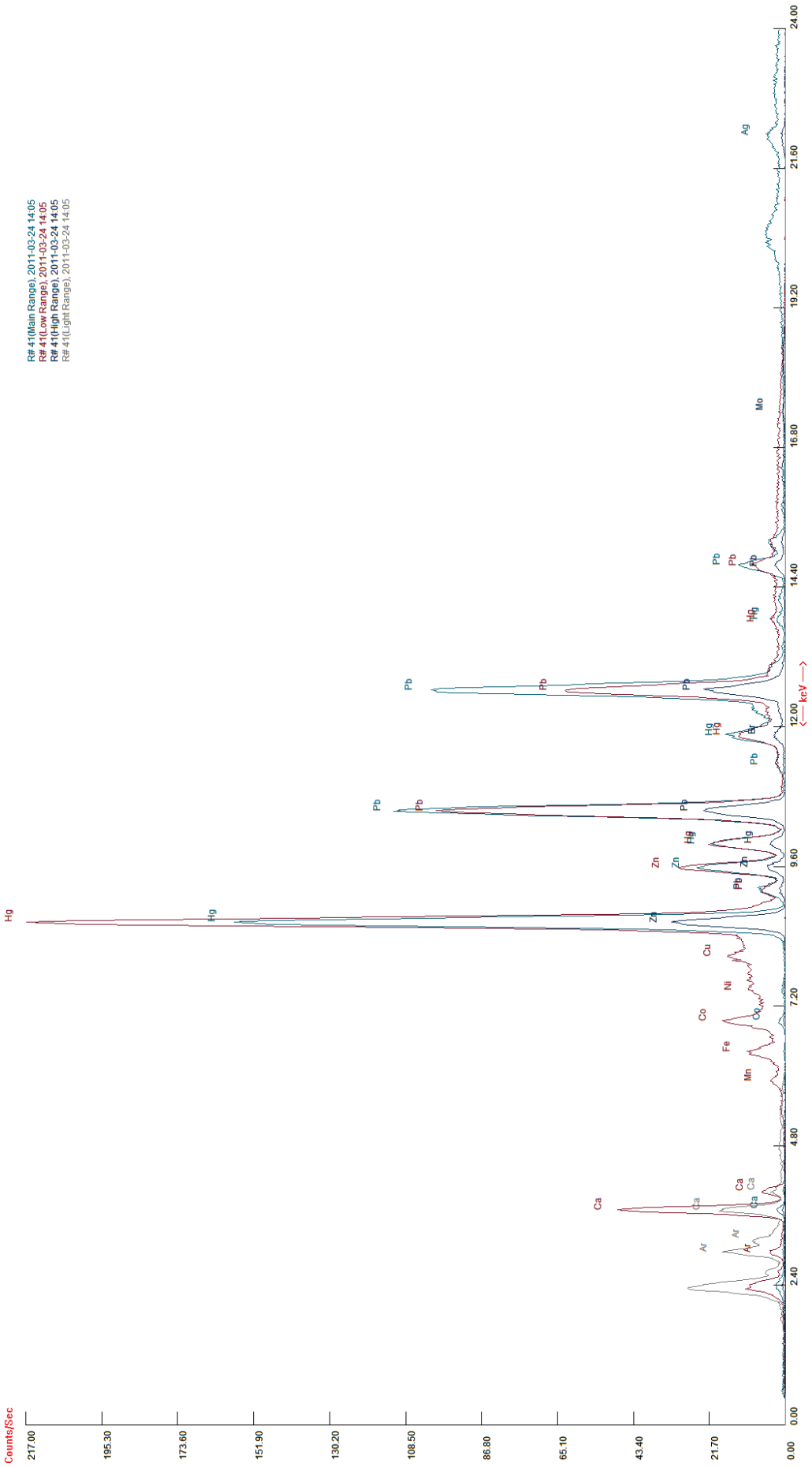

Kilden 4a.3

# APPENDIX 3: XRF SPECTRAS



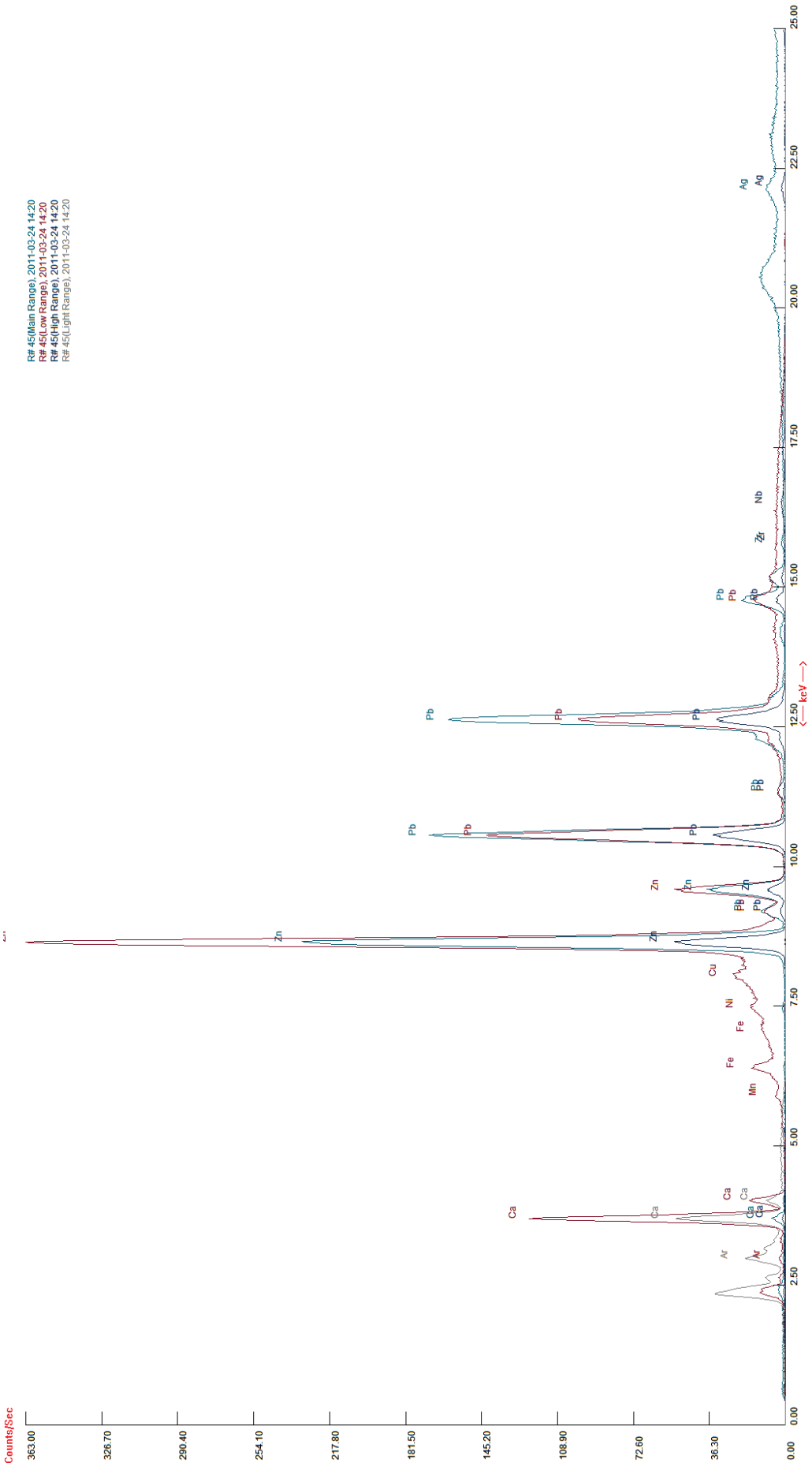

Kilden 4a.4

# APPENDIX 3: XRF SPECTRAS



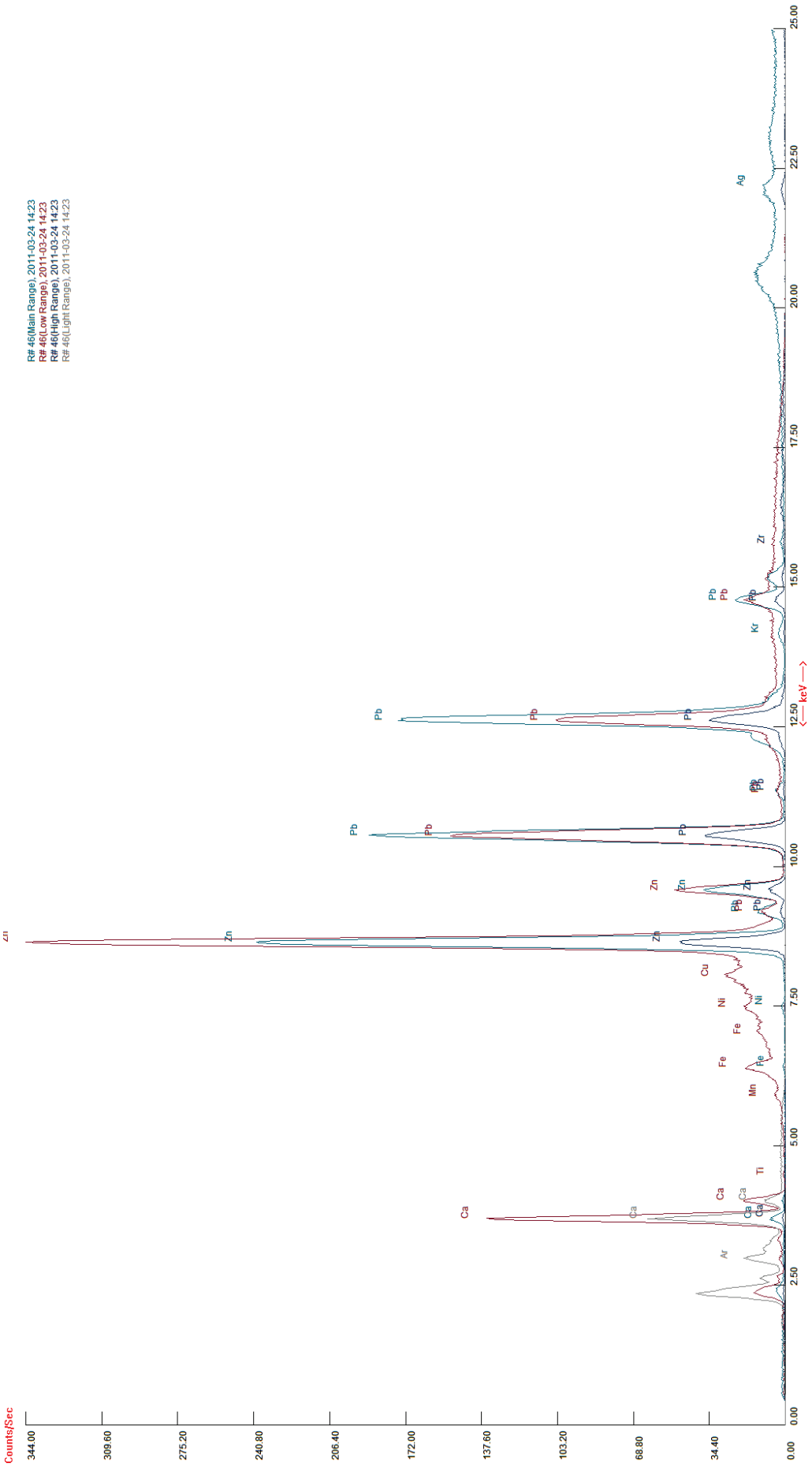

Kilden 4a.5

# APPENDIX 3: XRF SPECTRAS

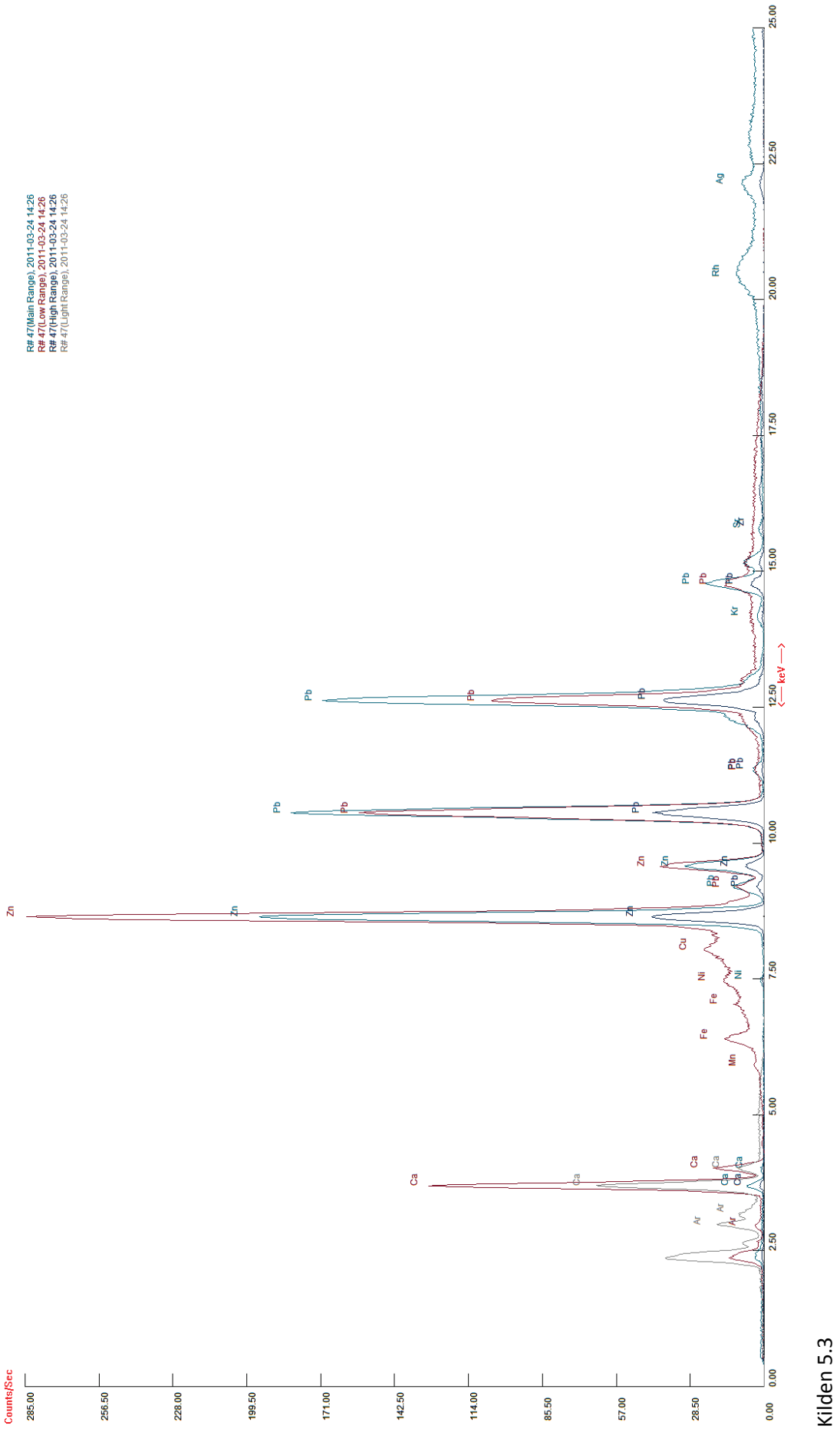



Kilden 5.1

# APPENDIX 3: XRF SPECTRAS

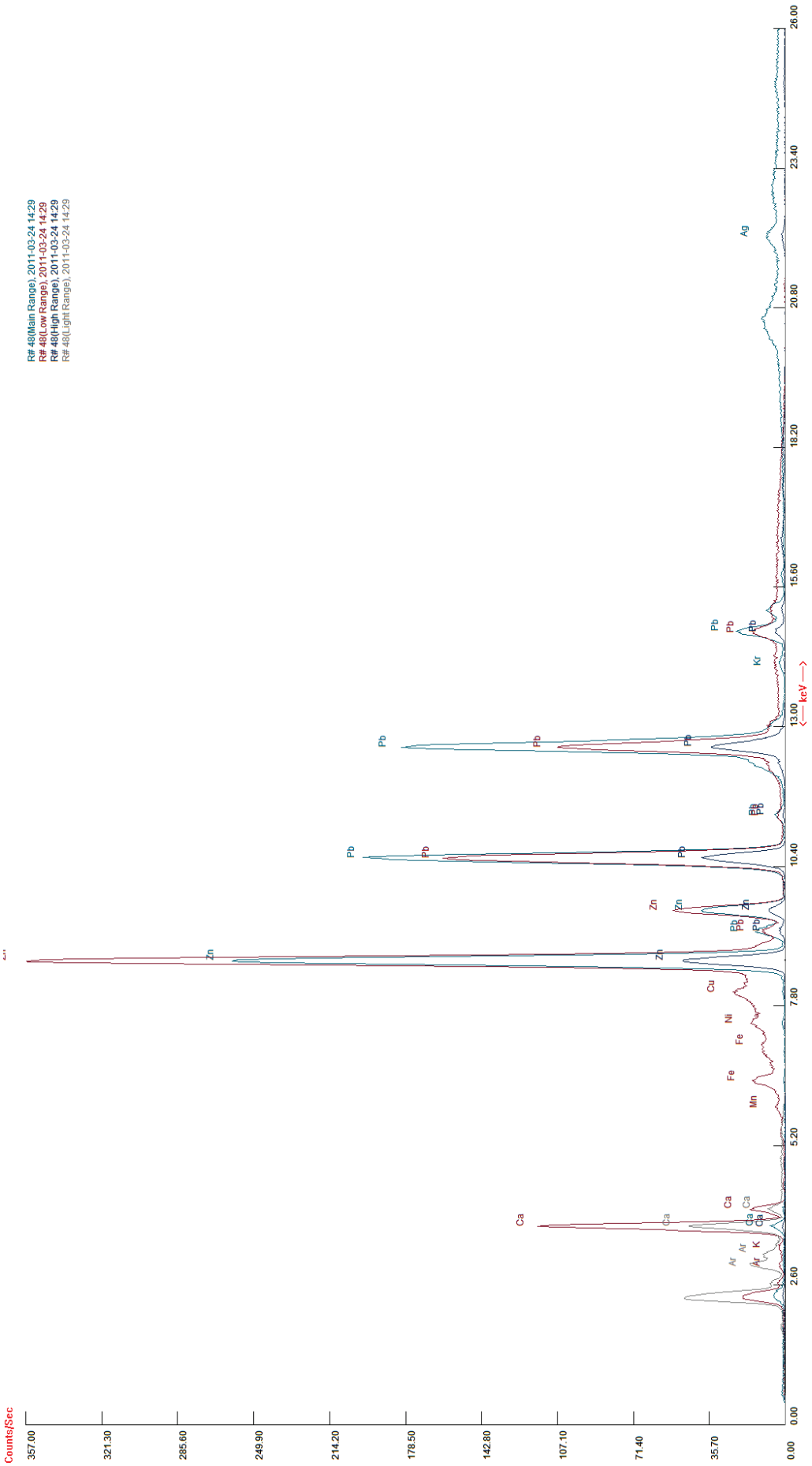


# APPENDIX 3: XRF SPECTRAS



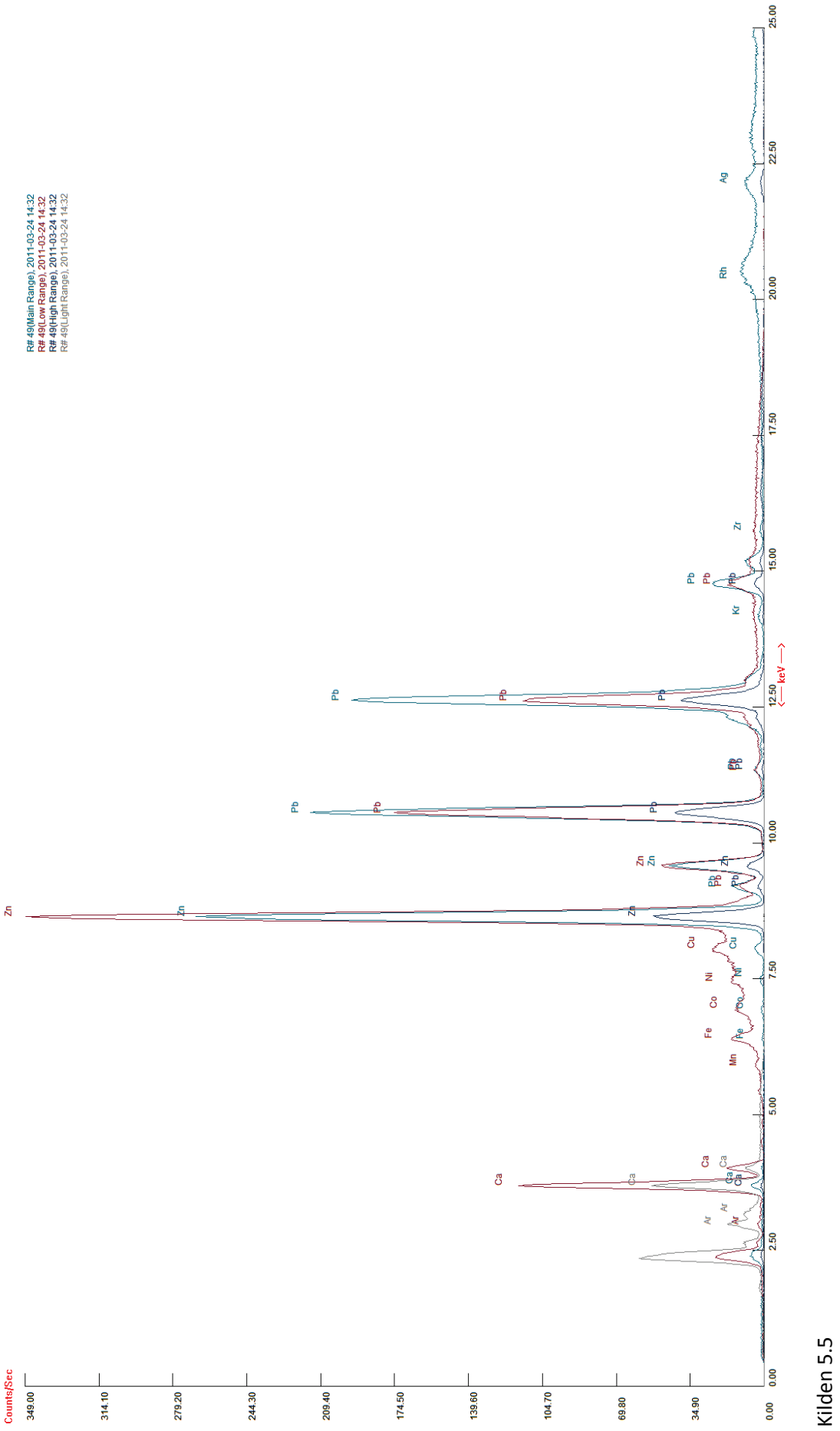

Kilden 5.3

# APPENDIX 3: XRF SPECTRAS



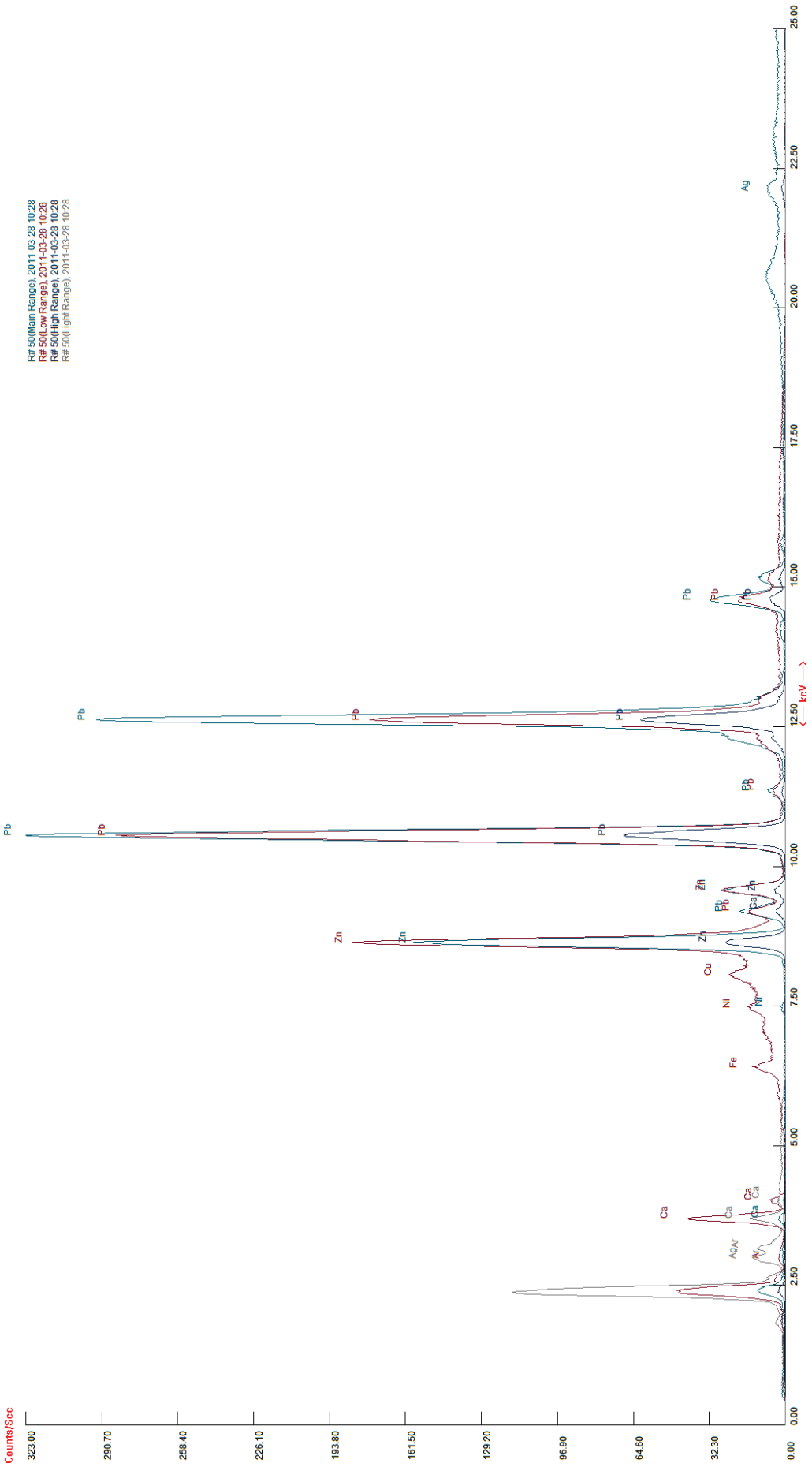

Kilden 5.4

# APPENDIX 3: XRF SPECTRAS



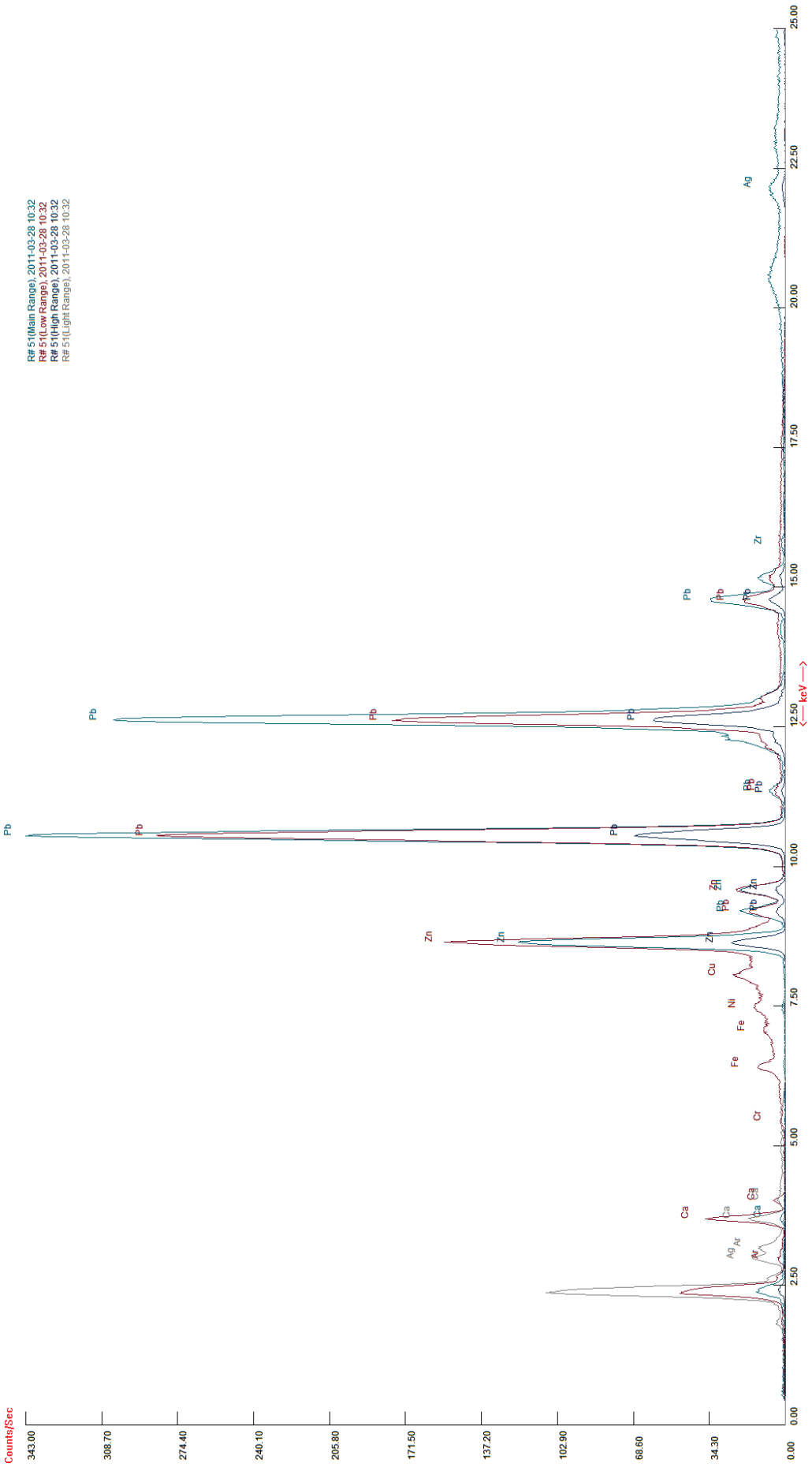

Kilden 5.5

# APPENDIX 3: XRF SPECTRAS



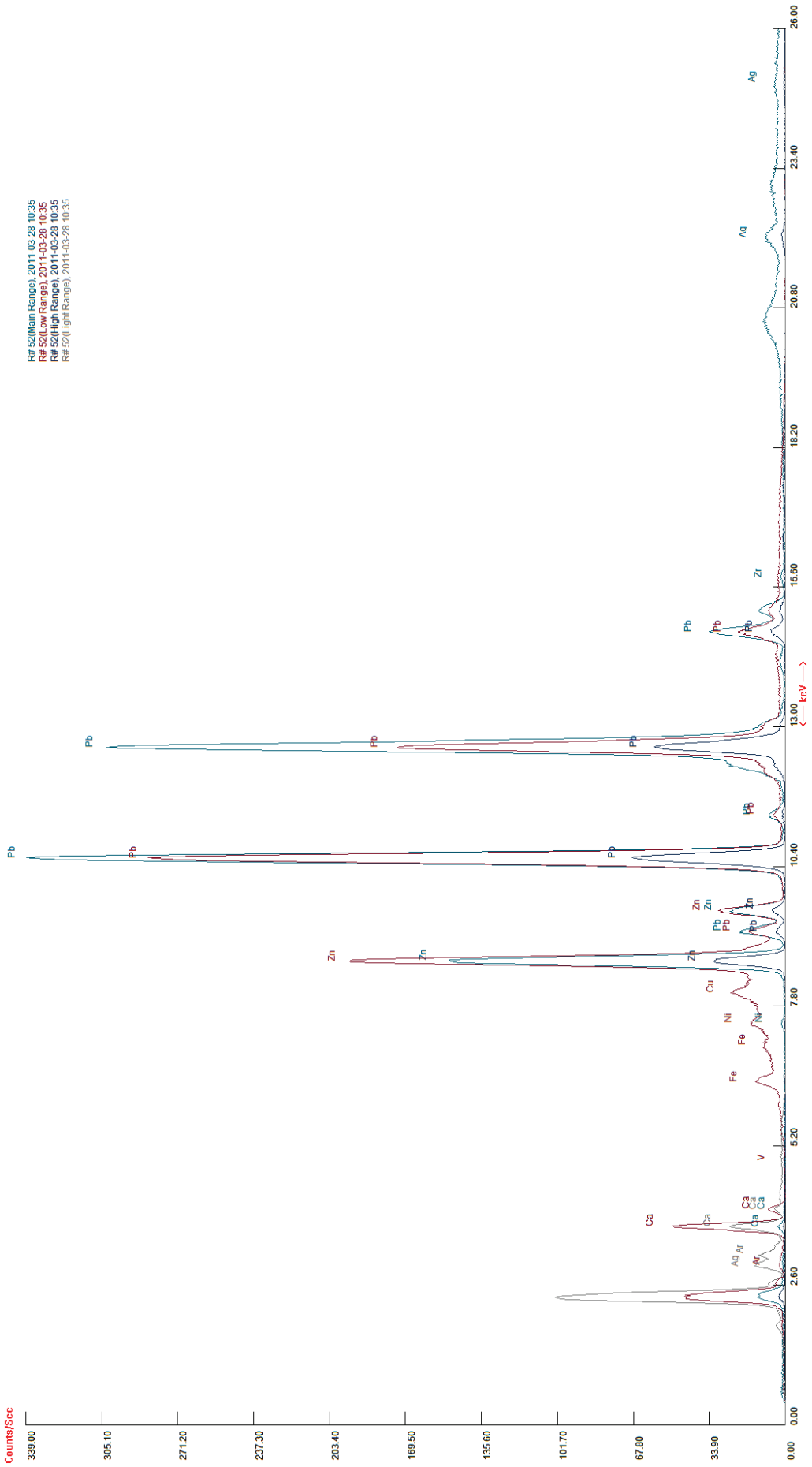

Kilden 6.1

# APPENDIX 3: XRF SPECTRAS



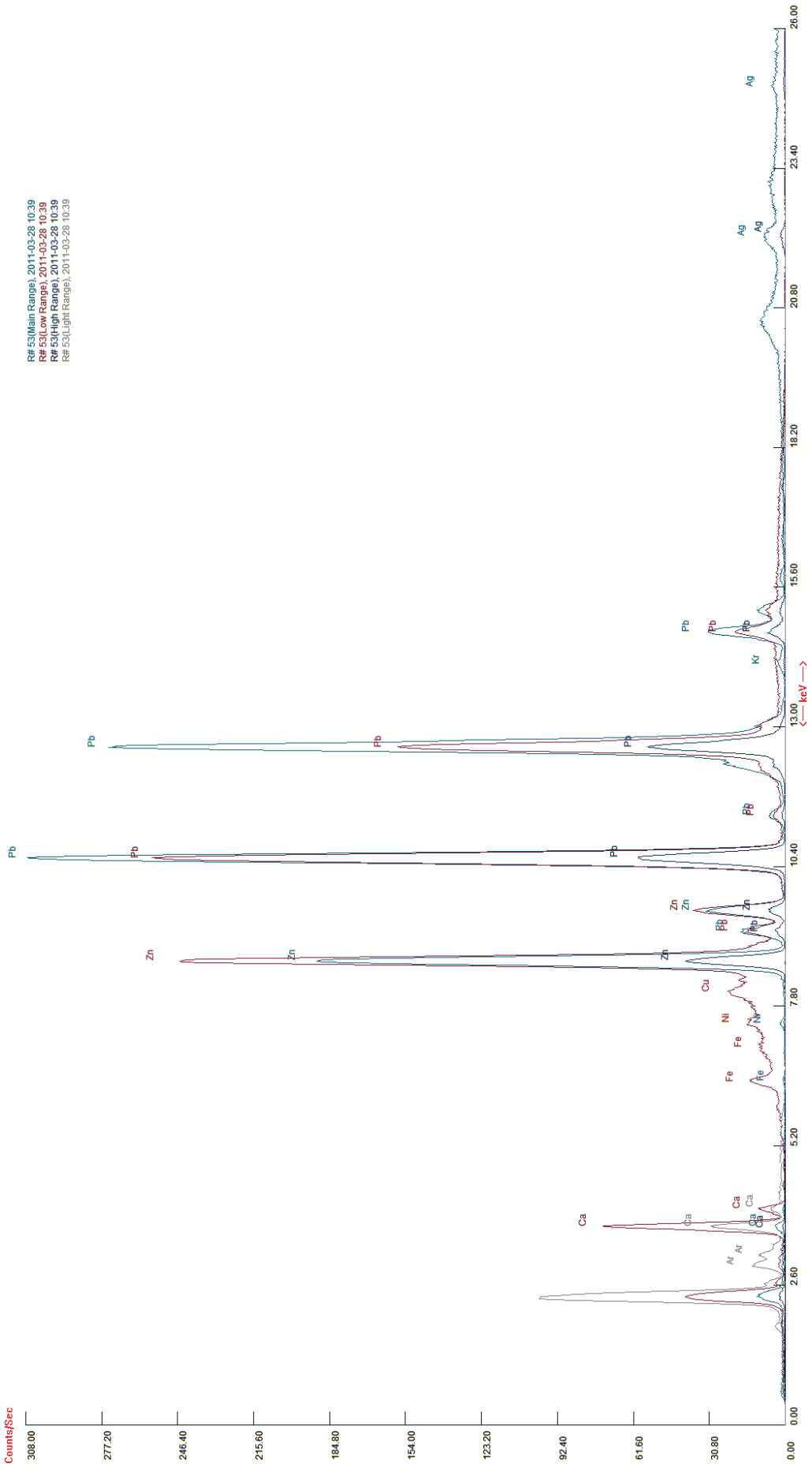

Kilden 6.2

# APPENDIX 3: XRF SPECTRAS



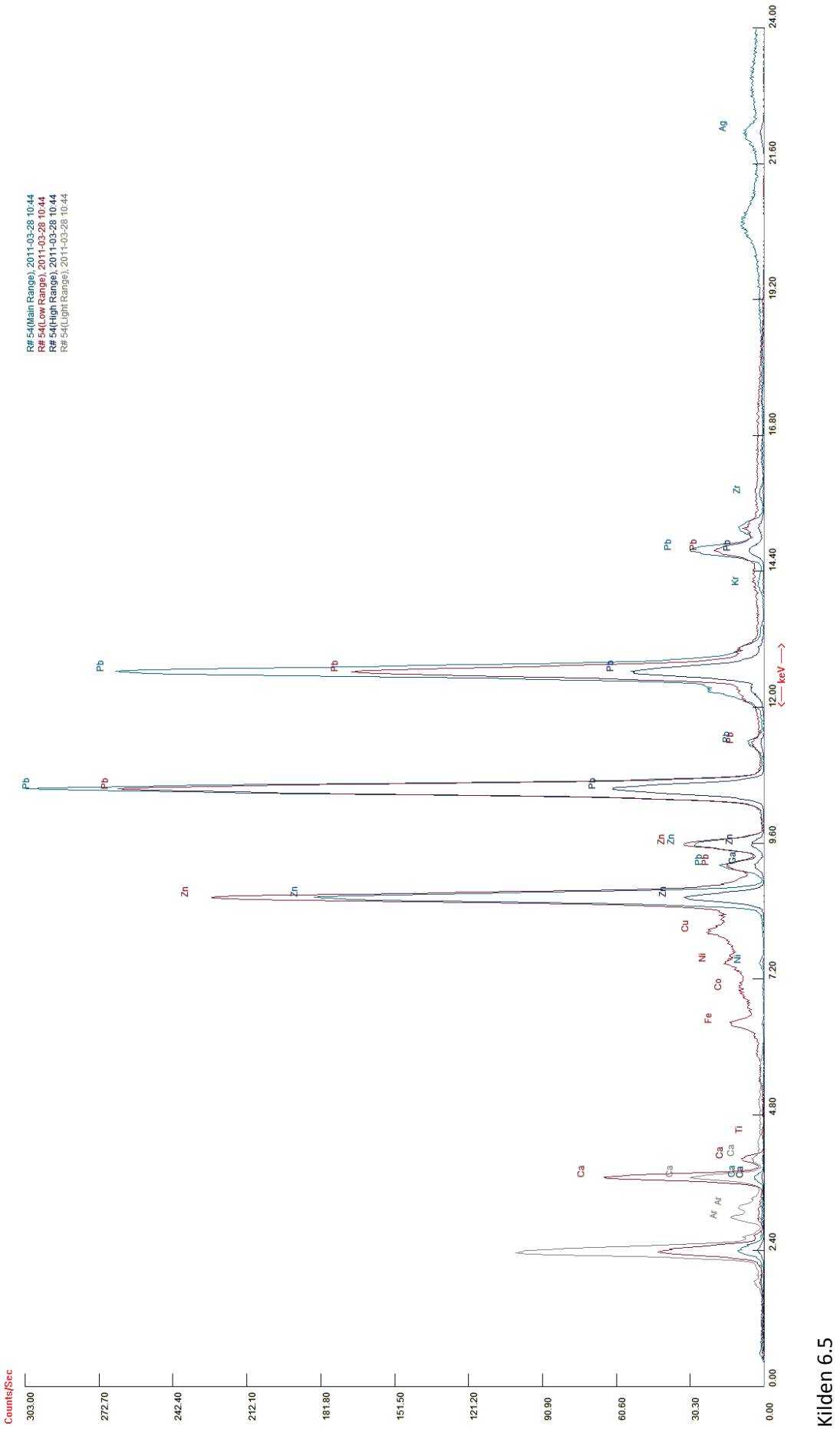

Kilden 6.3

# APPENDIX 3: XRF SPECTRAS

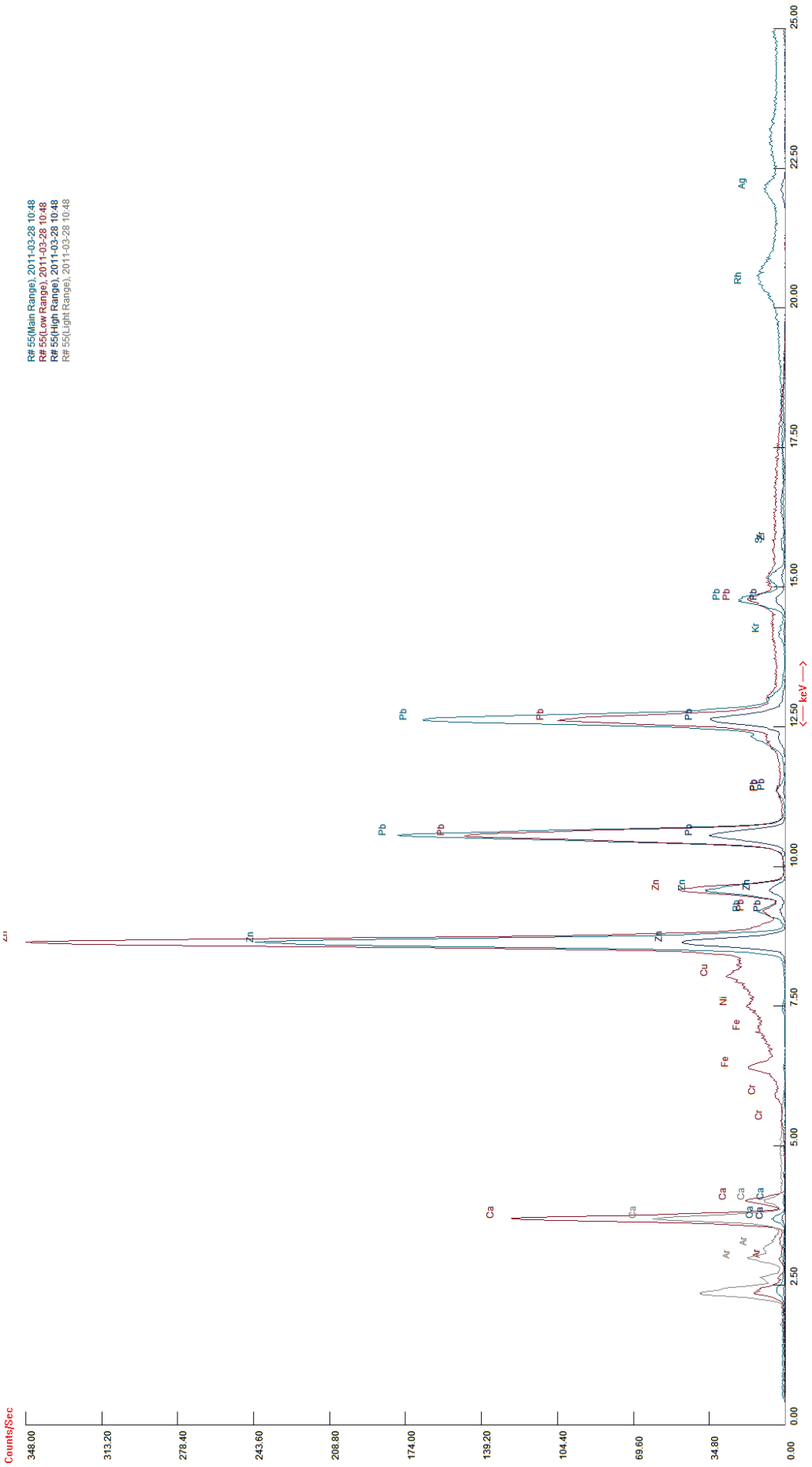



Kilden 6.4

# APPENDIX 3: XRF SPECTRAS

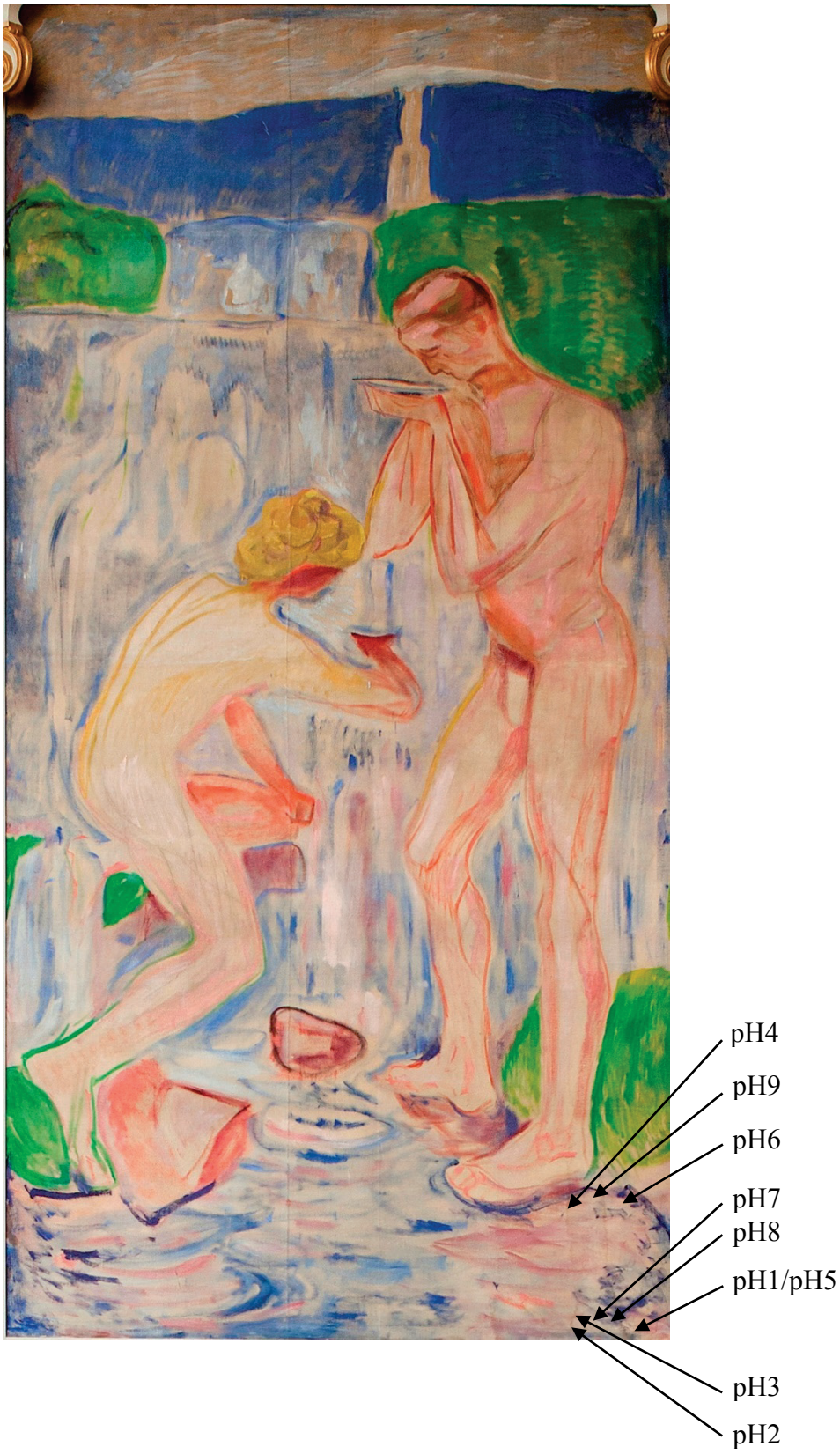


# APPENDIX 3: XRF SPECTRAS




Kilden 7 (bar grundering)

## APPENDIX 4: pH MEASUREMENTS OF TIDE-LINE AREAS



## APPENDIX 4: pH MEASUREMENTS OF TIDE-LINE AREAS

| | |
|---|---|
| pH1 (outside tide-line area): | 5.48 |
| pH2 (in border region of tide-line area): | 5.70 |
| pH3 (in border region of tide-line area): | 5.77 |
| pH4 (in border region of tide-line area): | 5.87 |
| pH5 (outside tide-line area): | 5.74 |
| pH6 (outside tide-line area): | 5.08 |
| pH7 (in middle of tide-line area): | 5.96 |
| pH8 (in middle of tide-line area): | 5.68 |
| pH9 (in middle of tide-line area): | 5.88 |

(pH measurements performed 26.02.2010)